June 15, 1943. G. F. NADEAU ET AL 2,322,048

NON-TACKY ADHESIVE COATED SHEETING

Filed June 10, 1938

FIG. 1

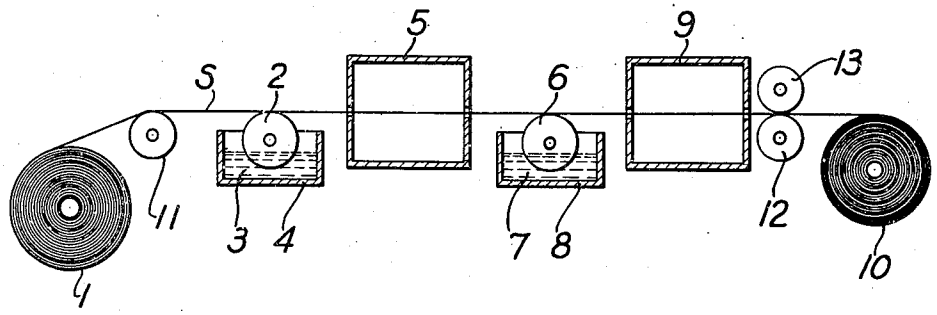


FIG. 2

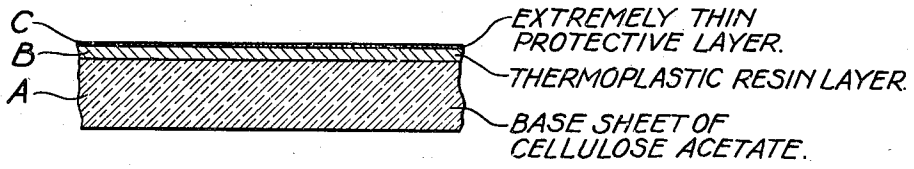
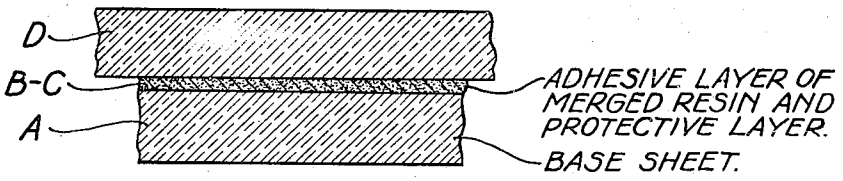


FIG. 3



Gale F. Nadeau
Clemens B. Starck
INVENTORS.

BY Newton M. Perrins
Daniel J. Mayne
ATTORNEYS

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NONTACKY ADHESIVE COATED SHEETING

Gale F. Nadeau and Clemens B. Starck, Rochester, N. Y., assignors to Eastman Kodak Company, Rochester, N. Y., a corporation of New Jersey

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6 Claims. (Cl. 117—73)

This invention relates to cellulosic sheeting and more particularly to a non-tacky, transparent cellulose derivative sheeting adapted for direct adhesion to surfaces by means of heat and pressure and without the use of cements or other special adhesives.

This application is in part a continuation of application Serial No. 68,696, filed March 13, 1936.

The sheeting art has long been familiar with the use of transparent sheeting for covering various objects, either as a wrapping tissue or in the form of relatively thicker material employed for the manufacture of cartons and the like. Such sheeting has also been used to protect printed surfaces, such as maps, identification cards and many similar articles. Printed transparent or semi-transparent labels made of this type of sheeting have also come widely into vogue for a variety of uses, especially as labels for bottled goods and as stickers for application to the windshields of automobiles. The most common types of such sheeting are composed of cellulosic or cellulose derivative materials, particularly cellulose acetate and similar relatively non-inflammable substances.

With this type of sheeting it has always been a problem to obtain the proper degree of adhesion between the sheeting and the surface to which it was to be attached. The usual types of water soluble adhesives alone are out of the question for the reason that water will not sufficiently wet this type of material. It has therefore been necessary to resort to special cements or to use special solvents with ordinary cements. Even these expedients have not proved satisfactory, since sheeting, especially the thinner varieties most commonly used for the above-mentioned purposes, are particularly susceptible to the action of solvents in the cementing medium and it is extremely difficult, if not impossible in a good many cases, to properly cement thin sheeting without wrinkling, shrinkage, and other types of distortion.

Not only has it been difficult to obtain proper adhesion, but also where adhesive layers of various kinds have been applied to cellulose derivative sheeting in an attempt to produce a quick-sealing product the sheeting is invariably tacky at ordinary temperatures and cannot be rolled upon itself or packed in the form of sheets laid one on top of the other, since the adhesive coating sticks to the underlying or overlying sheets. Such sheeting also has a tendency to lose its adhesive character upon aging and becomes brittle and otherwise unsatisfactory.

The ideal transparent thermoplastic or self-sticking sheet should, of course, be non-tacky at ordinary temperatures, should have the appearance, transparency and general characteristics of ordinary non-adhesive sheeting, and at the same time should be capable of being cemented to any type of surface, whether paper, wood, glass, metal, cellulosic or cellulose derivative or other material without the necessity of using either special cements or special technique.

The present invention has as its principal object to provide a non-tacky, cellulose derivative sheet material which may be permanently and adhesively joined to a surface without the use of special cements or special technique. A further object is to provide a thin transparent or semi-transparent cellulose derivative sheet adapted for protectively covering printed matter, photographs, book covers, and for a wide variety of similar uses. A still further object is to provide a type of thin, transparent, non-tacky cellulosic sheeting adapted for direct and adhesive union with wood, paper, metal, glass, or to cellulosic or cellulose derivative or other surfaces merely by the application of heat and pressure. Another and specific object is to provide a cellulosic or cellulose derivative sheet coated on one surface with a thin layer of thermoplastic adhesive resin, which layer, if unprotected, would render the sheet tacky and incapable of being rolled upon itself without adhesion and having over the resin layer a protective coating of almost imperceptible thickness of such nature as to render the sheet capable of being rolled upon itself without adhesion between contacting surfaces and yet capable, under the influence of heat and pressure of merging with the resin layer. Other objects will appear hereinafter.

These objects are accomplished by the following invention which, in its broader aspects, comprises applying to a thin, or relatively thin, cellulose acetate or other cellulosic base sheet, a thin coating of a thermoplastic resin and then applying over the resin coating an extremely thin coating of a material adapted to merge with the resin coating upon the application of heat and pressure and yet having the ability to protect the resin coating, even if inherently quite tacky, and both to render the coated sheet non-tacky and to enable it to be rolled upon itself without adhesion between contacting surfaces and to remain completely non-tacky at ordinary tempera-

tures and under ordinary conditions of use or storage, even in tropical countries.

In the following examples and description we have set forth several of the preferred embodiments of our invention, but they are included merely for purposes of illustration and not as a limitation thereof.

As a rule we prefer to use a cellulose organic acid ester material for the base sheet, such as a sheet of cellulose acetate or cellulose acetate propionate, although we may use almost any type of celulosic sheeting which is flexible or pliable and possesses the properties required for the purpose to which the material is to be put in actual use. The sheet may be coated with the resin by bead or other form of application from an appropriate solution in a volatile solvent, the resin coating superficially dried and the protective coat then applied in similar manner. If necessary, in order to give the resin coating any desired properties such as increased flexibility and the like, the resin solution may contain a plasticizer such as dimethyl phthalate or other well-known cellulose derivative plasticizers. After drying of the last coat, the sheeting may be wound upon itself and stored for use.

In the accompanying drawing:

Fig. 1 is a diagrammatic sectional elevational view of one type of apparatus in which the coating process may be carried out.

Fig. 2 is a greatly exaggerated section through a coated sheet.

Fig. 3 is another exaggerated section illustrating the manner of sticking the coated sheet to another surface.

The following examples will illustrate typical methods of carrying out the invention:

Example I.—Referring to Fig. 1 of the drawing, a sheet S of cellulose acetate of about .001 inch in thickness is passed from supply roll 1 into contact with applicator roll 2 which carries up and into contact with the under surface of the sheet an appropriate amount of the resin coating solution 3 contained in hopper 4. The solution consists of a non-heat hardening thermoplastic resin dissolved to a concentration of about 4–10% in a suitable solvent therefor, which solvent slightly attacks, or, at least softens or swells the cellulose acetate sufficiently to permit the resin to be tenaciously anchored thereto upon evaporation of solvent from the solution. A typical composition is a 5% methanol solution of alcohol-soluble polyvinyl acetate, such as that sold under the trade name Gelva. The solution may be applied at a coating speed of about 4–5 feet per minute.

The resin-coated sheet then passes to drier 5 where it is subjected to a mild drying temperature of about 140° F. for a period sufficient to eliminate solvents from the coating. From the drier 5 the sheet, which, with the resin layer or coating unprotected, would be tacky and incapable of being rolled upon itself without adhesion between contacting surfaces, is then passed into contact with applicator roll 6 which deposits thereon over the resin layer a 2–2.5% solution of low viscosity nitrocellulose, the nitrocellulose being plasticized by the addition thereto of 40% by weight of the ester of triphenyl phosphate. After the deposition of this layer the material passes through drier 9 where solvents are evaporated from the nitrocellulose coating, and thence the sheet passes to wind-up roll 10. If desired, guide rolls 11, 12, and 13 may be provided to facilitate handling the sheeting.

The layer of deposited resin when dry is of the order of .0001 to .0008 inch in thickness, although this may vary rather widely beyond these limits. The protective layer of cellulose derivative applied over the resin layer is of practically microscopic thickness, being of the order of only a few millionths of an inch, but nevertheless causes the sheet to be non-tacky and capable of being rolled upon itself and stored in rolls, even in a relatively warm atmosphere and for an indefinite length of time, without adhesion between the coated surface and any part of the material with which it comes in contact.

Example II.—A sheet of cellulose acetate propionate of the order of .003 inch in thickness is treated as described in Example I, the resin solution being a 10% solution of the resin sold under the trade name "Alvar" in a solvent mixture composed of 60% by weight acetone and 40% methyl alcohol, the coating operation being carried out at a speed of 6–8 feet per minute. After drying the resin-coated sheet is then treated by application of a composition having the following composition:

	Per cent
"Rezyl" #12 (a polyhydric alcohol-polybasic acid or alkyd resin)	0.5
Low viscosity cellulose nitrate	2.0
Acetone	25.0
Methanol	72.5

The dried product is substantially identical with the product of Example I.

Example III.—A cellulose acetate sheet is coated with a resin layer as described in the first paragraph of Example I. After drying of the resin layer there is applied thereover a composition of the following formula

	Per cent
Polyvinyl butacetal (residual polyvinyl acetate 2.7%—residual polyvinyl alcohol 8.0%)	4
Acetone	50
Methyl alcohol	46

It is found that, upon drying, the layer of polyvinyl acetal resin forms a microscopically thin covering, the protective function of which is substantially identical with the layer of cellulose nitrate of Example I or the layer of mixed cellulose nitrate and "Rezyl" of Example II.

Example IV.—A sheet prepared as described in the first paragraph of Example I is coated with a composition having the following formula:

	Per cent
Maizite (zein)	2
Ethyl alcohol	80
Water	18

Upon drying the resulting sheet material is found to have the same properties as the product of Example I.

Although a variety of resins may be employed for the thermoplastic layer or coating, we prefer to employ vinyl compounds, particularly the resins sold under the trade name "Gelva" (a polymerized form of vinyl acetate, the preparation of which is described in U. S. Patents 1,241,738, 1,586,803, and 1,710,825); "Alvar" (an acetal derived from the condensation of partially hydrolized polyvinyl acetate with acetaldehyde, the preparation of which is described in U. S. Patents 1,872,834 and 1,971,951); and "Formvar" (an acetal derived from the condensation of partially hydrolized polyvinyl acetate with formaldehyde, the preparation of which is described in

British Patent 351,082). Of such compounds, we prefer to employ one which contains a relatively high percentage of acetyl, since such high acetyl compounds are relatively more thermoplastic than those of lower acetyl content. Examples of other suitable resins are mixed acetals of polyvinyl alcohol, polyalkyl acrylates and polyalkyl methacrylates.

As indicated in the above examples we may employ a plurality of materials for producing the protective layer over the resin layer. In some instances we may find it desirable to employ a mixture of a cellulose derivative, such as a low viscosity cellulose nitrate and a resin, such as that sold under the trade name "Rezyl" or some other type of polybasic acid-polyhydric alcohol or alkyd resin. In such mixtures we may also employ a resin such as that sold under the trade name "Petrex-5" which is an alkyd type resin prepared from a polybasic acid of terpene origin and any of the usual types of polyhydric alcohols such as glycols and the polyglycols. In some instances we may even employ a resin of the type of "Alvar" in admixture with the cellulose nitrate component.

As indicated by Example III we may employ a resin alone, that is, without the use of any other additions such as cellulose nitrate or other cellulose derivative. A number of resins suitable for this purpose are, for example, "Alvar," a polyvinyl butacetal, the preparation of which is described in French Patent 808,586, or other acetal resins of this general nature, the preparation of which resins is described in U. S. reissue patent to Morrison et al. 20,430. Cellulose ethers may be used for this purpose. For example, an ethyl ether of approximately 40% ethoxy content has been found to produce a very satisfactory protective coating when deposited on the resin layer of the sheet from a 2–4% solution in methyl alcohol. In addition we may employ certain proteins such as casein, gelatin and zein. In fact, the broad scope of our invention includes the use of any suitable material which is capable of forming a thin protective layer over the resin layer and is capable of merging with the resin layer under the influence of heat and pressure but at the same time is capable of permitting the sheet material to be rolled upon itself and stored and handled even in a moderately warm atmosphere and for an indefinite length of time without adhesion between the resin coated surface and any other surface of the material with which it may come in contact.

It will be evident that many changes may be made in the above described coating procedure within the scope of the invention. The coating speed and/or the concentration of the coating solutions may be varied to give varying thickness of coatings. In general, if a thicker coating is desired, the speed of coating is increased, or the concentration of the coating solution is increased, or both expedients are employed.

While we have found it convenient to illustrate our invention by reference to the above method, it is obvious that other technique may be employed for depositing the resin and protective coatings. For example, when dealing with some of the extremely thin types of sheeting, especially those used for wrapping sheets and for protecting certain types of printed matter, it is extremely difficult to coat preformed sheeting, since it has an almost uncontrollable tendency to wrinkle and distort. For such material, we prefer to use the coating method illustrated in the U. S. patent to J. B. Wells, No. 2,036,377, wherein the coating solution is applied to the sheeting before it has been removed from the surface on which it is formed and while it is in a relatively "green" condition and contains an appreciable amount of residual solvent.

The product produced in accordance with our invention is illustrated in Fig. 2. A is the base sheet which may be composed of cellulose derivative material, such as cellulose acetate, cellulose propionate, cellulose butyrate, cellulose acetate propionate, or other suitable single or mixed ester of cellulose, regenerated cellulose, or similar material. B is the layer of thermoplastic resin, such as a polyvinyl acetate resin, while C is an extremely thin protective layer which may be composed of a cellulose derivative such as cellulose nitrate or cellulose acetate or any of the other materials indicated above as capable of functioning to protect the resin layer, i. e., to render the sheet non-tacky and capable of being rolled upon itself and stored without adhesion of contacting surfaces. The thickness of the various layers may vary within wide limits. For example, the base sheet may be relatively thin, say of the wrapping tissue type of about .0008–.001 inch in thickness or less, or it may be of relatively thicker material, say of the order of .003–.005 inch or more, designed to withstand severe usage, as in the formation of transparent boxes or containers or window elements in cartons and for the protection of photographic prints. Likewise, the thickness of the resin layer may vary widely, although it may be said in general that the resin coating is preferably rather thin in order to avoid an excess of adhesive material on the sheet. The protective layer is of almost imperceptible thickness and is kept as thin as possible, since it must eventually merge readily with the underlying resin layer. As stated, its function is to cover the resin and form a protective covering thereover to render the finished sheeting non-tacky and thus permit of its being readily handled and rolled upon itself in storage.

If a cellulose derivative is employed for the protective coating, it is preferably composed of cellulose nitrate of low viscosity containing a relatively high percentage of placticizer in order to render the material plastic at moderately elevated temperatures and thus permit it to merge with the underlying resin coating when the sheet is adhesively joined to another material. The plasticizer may represent 15–50 or even 60% by weight, or more, of the weight of the cellulose derivative. Other cellulose derivatives such as cellulose acetate, cellulose propionate or cellulose acetate propionate and the like may also be employed for the protective coating, the material being relatively highly plasticized, as in the case of cellulose nitrate. Where other protective materials are employed as herein set forth, appropriate plasticizers will be used if desired and in an amount sufficient to render the coating capable of softening readily under heat and pressure and of merging with the underlying resin layer.

The sheeting is preferably transparent, but it may be translucent only, or even opaque. The surface opposite the resin and protective coatings may be specially treated to permit writing or printing thereon or it may be moistureproofed, if desired, as by the application of a gum-wax moistureproofing composition in accordance with the technique described and claimed in the U. S. patent to Beach 2,166,711 or other technique.

The sheeting of our invention is distinguished from all similar products of the prior art by the fact that, notwithstanding the thermoplastic character of the resin coating, it is completely non-tacky and capable of being rolled upon itself and stored, even in a relatively warm atmosphere, without adhesion between contacting surfaces. As previously indicated, one of the most serious problems met with in the use of resinous materials as thermosensitive adhesives is the tackiness of the coated sheet material. In fact, practically all resins which are susceptible of use in heat laminating operations are so inherently tacky as to preclude their use on sheet material which is to be rolled upon itself or cut into sheets and stacked for future use. The art has long sought a thermoplastic sheet, that is, a sheet having thereon an adhesive coating which would respond to heat and pressure, yet would be capable of rolling or cutting and stacking without disastrous results. In the present material we have provided such a sheet and, in fact, have by the use of our protective overcoat on the resin layer produced a commercially practical product. Furthermore, we have thus made available a wide variety of valuable thermoplastic resins for the purpose of heat lamination of sheet materials which were hitherto impractical if not impossible, to use due to their inherent tackiness.

In use the resin-coated sheeting of our invention is simply applied with the coated side in contact with the surface to which it is to be adhesively joined and moderate heat and pressure are applied. The result is illustrated in Fig. 3. The protective layer C breaks through into the resin layer B, these layers thus merging to form a single adhesive layer B—C between the base sheet A and the surface D.

The product of our invention has a wide variety of uses, among which may be mentioned labels for sticking to almost any type of surface, including paper, cardboard, wood, metal, and glass. It finds particular application in the manufacture of stickers, of labels for automobile windshields, the material readily sticking to glass, porcelain or similar materials. An especially valuable application is in the bookbinding art where it may be used for the manufacture of protective transparent covers for books, especially children's books. The material may also be applied as a protective covering for, or to give a glossy finish to maps, prints, and various other articles. In fact, it is possible to simulate closely a photograph by laminating over an ink print a sheet of our material. The superposed sheet produces a rich gloss and depth of tone which is indeed remarkable and unexpected. Inasmuch as the material is provided with adhesive it may readily be employed in the manufacture of laminated cartons, particularly of the so-called window type, by laying it over the pasteboard or other blank or form and simply applying moderate heat and pressure, one such application being described and claimed in the U. S. patent to McGrady 2,218,246. Many other uses will be apparent to those skilled in the art.

What we claim is:

1. A non-moistening sheet material which is non-tacky at ordinary temperatures but capable of being adhesively joined to the surface merely by application of heat and pressure, comprising a pliable, transparent, cellulose organic acid ester base sheet coated on one surface with a thin layer of an adhesive resin which is thermoplastic at a temperature below the fusion point of the cellulose ester sheet, which layer, if unprotected, would render the sheet tacky and incapable of being rolled upon itself without adhesion, a non-tacky protective coating composed of a cellulose ester containing a plasticizer therefor of almost imperceptible thickness, said layer being superimposed on the resin layer and rendering the sheet capable of being rolled upon itself without adhesion, which under the influence of heat and pressure merges with the resin layer without substantialliy reducing the adhesive power thereof.

2. A non-moistening sheet material which is non-tacky at ordinary temperatures but capable of being adhesively joined to the surface merely by application of heat and pressure, comprising a pliable, transparent, cellulose acetate base sheet coated on one surface with a thin layer of an adhesive resin which is thermoplastic at a temperature below the fusion point of the cellulose acetate sheet, which layer, if unprotected, would render the sheet tacky and incapable of being rolled upon itself without adhesion, a non-tacky protective coating composed of a cellulose ester containing a plasticizer therefor of almost imperceptible thickness, said layer being superimposed on the resin layer and rendering the sheet capable of being rolled upon itself without adhesion, which under the influence of heat and pressure merges with the resin layer without substantially reducing the adhesive power thereof.

3. A non-moistening sheet material which is non-tacky at ordinary temperatures but capable of being adhesively joined to the surface merely by application of heat and pressure, comprising a pliable, transparent, cellulose acetate base sheet coated on one surface with a thin layer of an adhesive vinyl resin which is thermoplastic at a temperature below the fusion point of the cellulose acetate sheet, which layer, if unprotected, would render the sheet tacky and incapable of being rolled upon itself without adhesion, a non-tacky protective coating composed of a cellulose ester containing a plasticizer therefor of almost imperceptible thickness, said layer being superimposed on the resin layer and rendering the sheet capable of being rolled upon itself without adhesion, which under the influence of heat and pressure merges with the resin layer without substantially reducing the adhesive power thereof.

4. A non-moistening sheet material which is non-tacky at ordinary temperatures but capable of being adhesively joined to the surface merely by application of heat and pressure, comprising a pliable, transparent, cellulose acetate base sheet coated on one surface with a thin layer of a polyvinyl acetate resin which is thermoplastic at a temperature below the fusion point of the cellulose acetate sheet, which layer, if unprotected, would render the sheet tacky and incapable of being rolled upon itself without adhesion, a non-tacky protective coating composed of a cellulose ester containing a plasticizer therefor of almost imperceptible thickness, said layer being superimposed on the resin layer and rendering the sheet capable of being rolled upon itself without adhesion, which under the influence of heat and pressure merges with the resin layer without substantially reducing the adhesive power thereof.

5. A non-moistening sheet material which is

non-tacky at ordinary temperatures, but capable of being adhesively joined to the surface merely by application of heat and pressure, comprising a pliable, transparent, cellulose acetate base sheet coated on one surface with a thin layer of a polyvinyl acetal resin which is thermoplastic at a temperature below the fusion point of the cellulose acetate sheet, which layer, if unprotected, would render the sheet tacky and incapable of being rolled upon itself without adhesion, a non-tacky protective coating composed of a cellulose ester containing a plasticizer therefor of almost imperceptible thickness, said layer being superimposed on the resin layer and rendering the sheet capable of being rolled upon itself without adhesion, which under the influence of heat and pressure merges with the resin layer without substantially reducing the adhesive power thereof.

6. A non-moistening sheet material which is non-tacky at ordinary temperatures but capable of being adhesively joined to a surface merely by application of heat and pressure, comprising a pliable, transparent, cellulose acetate base sheet coated on one surface with a thin layer of an adhesive resin which is thermoplastic at a temperature below the fusion point of the cellulose acetate sheet, which layer, if unprotected, would render the sheet tacky and incapable of being rolled upon itself without adhesion, a non-tacky protective coating of cellulose nitrate containing a plasticizer therefor of almost imperceptible thickness, said layer being superimposed on the resin layer and rendering the sheet capable of being rolled upon itself without adhesion, which under the influence of heat and pressure merges with the resin layer without substantially reducing the adhesive power thereof.

GALE F. NADEAU.
CLEMENS B. STARCK.