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PRESSURE SEALING MEMBRANE

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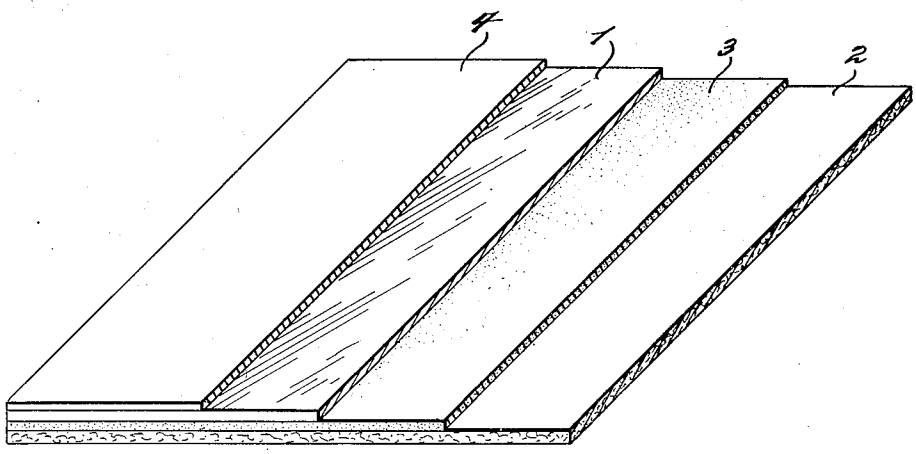

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PRESSURE SEALING MEMBRANE

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This invention relates to a sheet or film with adhesive on one side thereof and a material repellent to said adhesive on the other side.

A transparent film of this character may be used in covering the surface of paper or the like in order to protect such surface, to improve the decorative effect, or both. It is desirable that the finished coated surface be relatively hard, smooth, water-repellent, transparent, colorless, and that it maintain its transparency and colorlessness over a long period of time. It is also desirable that the film may be applied to the paper or other similar surface merely by the use of a moderate amount of pressure, such as that which might be produced by hand. The adhesive should be such that with this moderate amount of pressure the adhesion between the film and the surface to which it is applied shall be so great that an attempt to separate the film from the surface will result in the destruction or partial destruction of one or the other. The quality of an adhesive which permits relatively strong adhesion with only a moderate amount of pressure application will be called herein "pressure sealing." This quality or characteristic should be distinguished from what is known in the art as a "pressure sensitive" characteristic. "Pressure sealing" as used herein means a seal of a permanent nature.

With the use of adhesives of the pressure sensitive type, the two surfaces joined together may be separated without destruction of either. This is usually the result desired to be obtained with adhesives of this kind, which are often used on tapes and films which it is desired to remove after they have served their purpose. Applicant's film and adhesive, on the other hand, is of such a character that it cannot be removed without destruction of the film or surface to which the film is attached.

In handling film of the kind which is the subject matter of this invention, it is desirable to roll the film into rolls or stack it sheet upon sheet and it is necessary when so doing to interpose some kind of a repellent layer between the back of the film and the adhesive so that the two will not stick together. In applicant's invention, this is accomplished by coating the back of the film with a so-called "repellent," that is, a substance which is repellent to the adhesive and to which the adhesive will not adhere. For this reason, a cold lamination, that is, one carried out at room temperature, which is different from one in which heat is necessary, has a distinct advantage. Any form of so-called hot lamination or any use of a thermoplastic adhesive, or any adhesive which for any reason, such as the drying out of solvent, requires that heat shall be applied to the sheet of paper, necessarily changes the moisture content of that sheet with the result that that sheet in re-absorbing its normal moisture content, will necessarily absorb it only on one side, since it cannot absorb through the moisture-proof film. The resulting increasing dimensions of the sheet invariably cause curling of the paper. While this curling may be overcome by known methods, one of these methods at least involves a similar lamination applied to the opposite side of the sheet, thus doubling the cost.

Applicant's film may be used as an ornamental covering for paper, printed or otherwise, cardboard, fabrics, as a covering for checks to prevent tampering therewith, as a covering for old documents which might otherwise become torn or mutilated, and for such uses it is necessary not only to produce a film, adhesive, and repellent which will act as a proper protection and will stay on the surface to which it is applied, but it is also necessary to produce such substances which are substantially perfectly transparent in combination layer upon layer and to maintain that transparency over a relatively long period of time, even though the film be subjected to the oxidizing effect of light rays, whether natural or artificial.

It is a further object of the invention to provide a product of the character described in which the adhesive, sheet, and repellent and the various components thereof all have properties which are mutually incompatible or antagonistic to an extent necessary to prevent any undesired action or reaction therebetween to an extent which would impair the desirable properties of the product.

It is a further object of the invention to provide solvents used in the application of the adhesive which will be non-solvent, not only for the sheet, but also for the repellent.

It is a further object to provide solvents used in the application of the repellent which will be non-solvent, not only for the sheet but also for the adhesive.

It is a further object to remove as completely as possible all excess solvents in the drying process which follows the application of both the repellent and the adhesive so that no trace of either the repellent solvent or the adhesive solvent is left in the finished product.

It is a further object to provide a composite sheet of the character described free of all solvents as initially manufactured and before rolling.

The accomplishment of the above and other objects will be set forth in the following description taken in conjunction with the accompanying drawing which shows diagrammatically a structure illustrating the present invention.

In the drawing, 2 represents the surface to be protected, e. g., a sheet of printed paper or the like. 1 shows the sheet of flexible transparent material united to 2 by a coating or film of a permanently pressure sealing adhesive 3. 4 shows

the repellent coating. The primary purpose of the latter is to permit the flexible transparent sheet, carrying the adhesive, to be rolled and readily unrolled.

Flexible transparent sheet materials in general may be used, including vinyl polymers. Esters and ethers of cellulose or regenerated cellulose may be used. The preferred material is cellulose acetate. The particular composition of the flexible sheet material is not important provided it possesses the desired qualities of transparency, flexibility, and stability toward moisture and sunlight. It should also be inert to the constituents of the adhesive and repellent and the solvents used in their application.

In accordance with the invention, the sheet of flexible transparent sheet material carries on one side a hydrophobic film of a permanently pressure sealing adhesive and on the other side a repellent to said adhesive, said repellent being, preferably, a surface-tension-lowering substance incorporated with a hydrophilic film-forming substance.

The adhesive may comprise two components, one a cohesion-producing agent and the other a tack-promoting agent. Each of these agents is substantially hydrophobic in character and the nature and proportions thereof are adjusted as hereinafter more fully described, to produce an adhesive of a permanently pressure-sealing character so that when the flexible transparent material is united with the surface to be protected, through the agency of the adhesive, separation cannot ordinarily be effected without destruction of either one of the surfaces joined together, e. g., either the destruction of flexible transparent material or the surface which it is intended to protect. Both the cohesion-producing agent and the adhesion-producing agent must be stable at least in the sense of resistance to the action of sunlight and moisture and must also be substantially colorless in thin films.

Generically, therefore, the hydrophobic film-forming material used as the cohesion-producing agent comprises a high molecular weight polymer substantially colorless in thin films and possessing little or no unsaturation; that is to say, a high molecular weight polymer which is not only colorless in thin films, but is also stable against the influence of light, air, and moisture. Among such cohesion-producing hydrophobic film-forming materials, the polymers known as polybutenes may be mentioned. These, while rubber-like in nature and possessing a high degree of intermolecular cohesion, are nevertheless substantially saturated and therefore stable in the sense of resistance to changes under the influence of light, air, and moisture. They may be obtained with various degrees of polymerization indicated by the molecular weight, which may be measured by the Staudinger viscosity method. Various grades, such as low, medium, and high, corresponding to molecular weights of 3,000–20,000, 80,000–115,000, and 200,000–400,000, for example, are indicative of the varying molecular weights which may be employed in accordance with the invention. The medium and high molecular weight products may be employed separately or may be incorporated with the low molecular weight product.

Another example of a suitable hydrophobic film-forming material possessing the necessary color characteristic and stability is typified by the acrylic polymers, as, for example, the material sold under the name "Acryloid," methyl methacrylate polymers, normal and isobutyl methacrylate polymers.

In accordance with the invention, the hydrophobic film-forming cohesion-producing agent may be advantageously incorporated with a hydrophobic film-forming tack-promoting agent, and the outstanding property required in this material, in addition to the property of imparting the necessary adhesion to the composition, is the property of stability. Among the material that may be employed for this purpose, the substantially saturated hydrocarbon resins produced by the hydrogenation of terpene polymers, hydrogenated dihydronaphthalene resin and hydrogenated coumarone-indene polymers measure up to the requirements of tack-promoting function and stability. The terpene polymers are obtained by the polymerization of unsaturated turpentine distillates, more especially that constituent thereof known as beta-pinene. By the application of hydrogenation to the polymers obtained, the unsaturation is reduced or eliminated and a stable hydrocarbon resinous product is obtained which may be incorporated with the cohesion-producing agent to obtain the necessary qualities. Such hydrogenated terpene polymers are sold under the name "Piccolyte WW." See U. S. Patent 2,249,112 to Carmody.

Other hydrophobic stable tack-promoting agents which may be employed are hydrogenated coumarone-indene resins and hydrogenated ester gum. The hydrogenated coumarone-indene resins, as the term describes, are obtained by the hydrogenation of the well-known coumarone-indene resins, as, for example, in the manner described in Carmody U. S. Patent 2,139,722. The hydrogenation confers the necessary stability and also contributes to the light color of the resin. Hydrogenated ester gum, as the term also describes, is produced by the glycerol esterification of hydrogenated rosin. Here again the hydrogenation imparts the necessary qualities of stability and color.

As previously explained, the adhesive, in accordance with the present invention, must possess, not only the property of intermolecular cohesion, but also intersurface adhesion. This combination of properties will be further explained as follows:

When the flexible transparent sheet material is provided with a film of adhesive and then united to the surface to be protected, as, for example, paper, the intersurface adhesion must be so great that separation of the flexible transparent material, e. g., cellulose acetate, and the paper cannot be effected without destruction either of the transparent sheet material or the paper. At the same time, the intermolecular cohesion of the adhesive must be so great as to approach as nearly as possible an integral bond between the flexible transparent material, e. g., cellulose acetate, and the paper to be protected, or, stated otherwise, the cohesion between the molecules of the adhesive must be so great as to offer a high degree of resistance to separation or movement.

The proportion of cohesion-producing agent to adhesion-producing agent varies with the degree of polymerization of each of these agents. The degree of polymerization of the cohesion-producing agent can be expressed in terms of its molecular weight, and the degree of polymerization of the adhesion-producing agent in many cases can be expressed in terms of its melting point.

The following table shows the effect of varying the relative proportions of the cohesion—and adhesion—producing agents, the term Vistanex being employed here to identify a polybutene having a molecular weight of about 95,000 and the term "resin" identifying a hydrogenated terpene polymer known as Piccolyte WW.

Vistanex (molecular weight 95,000)	Resin, M. P. 35° C.	Adhesion to calendered paper on lamination	Cohesion
Per cent	*Per cent*		
80	20	Poor	Good.
70	30	Fair	Do.
60	40	Fair to good	Do.
50	50	Good	Good to fair.
40	60	do	Fair.
30	70	Very good	Fair to poor.

For given proportions of a cohesion-producing agent having a definite molecular weight and adhesion-producing agents having different melting points, the melting point of the latter is of importance. For example, employing equal parts by weight of polybutene polymer of 95,000 molecular weight and hydrogenated terpene polymers having melting points of 60° C. and 115° C., the resin having a melting point of 60° C. produced an excellent adhesive, whereas the resin having a melting point of 115° C. produced an adhesive having less desirable qualities. By "excellent" is meant aggressive adhesive which will have a very strong bond to paper.

To summarize, therefore, the composition of the permanently-pressure sealing adhesive in accordance with the present invention may comprise a cohesion-producing polymer incorporated with an adhesion-producing polymer, each of these polymers being a hydrophobic film-forming substance of a substantially saturated character resistant to sunlight, moisture, and air and therefore stable for the purposes of the present invention.

For the purpose of illustration, the following examples are provided showing the character and composition of the total solids in the adhesive.

Example 1

	Per cent
Polybutene polymer, 95,000 molecular weight (Vistanex)	57.3
Polybutene polymer, 7,000 molecular weight	10.3
Hydrogenated terpene polymer (Piccolyte WW resin)	32.4

Example 2

	Per cent
Polybutene polymer, 95,000 molecular weight (Vistanex)	70.0
Hydrogenated coumarone-indene resins (Nevillite "V" M. P. 28–33° C.)	30.0

Example 3

	Per cent
Polybutene polymer, 95,000 molecular weight (Vistanex)	56.0
Hydrogenated coumarone-indene resin (Nevillite "V" M. P. 18–23° C.)	10.2
Hydrogenated coumarone-indene resin (Nevillite "V" M. P. 145–155° C.)	25.4
Polybutene polymer, 7,000 molecular weight (Vistanex)	8.4

Example 4

	Per cent
Acrylic polymer (Acryloid A–130)	55.6
Hydrogenated ester gum (Staybelite #10)	22.2
Russian mineral oil	22.2

Example 5

	Per cent
Acrylic polymer (Acryloid A–130)	46.3
Hydrogenated ester gum (Staybelite #10)	18.5
Russian mineral oil	18.5
Hydrogenated terpene polymer (Piccolyte WW)	16.7

Example 6

	Per cent
Isobutyl methacrylate polymer	66.6
Amyl stearate	33.4

Example 7

	Per cent
Vinylite AYAB vinyl acetate polymer	75
Kronisol (dibutoxy ethyl phthalate)	25

Example 8

	Per cent
Normal butyl methacrylate	55
Isobutyl methacrylate	20
Flexol 3GO (triethylene glycol di-2-ethyl hexoate)	20
Hydrogenated ester gum	5

Example 9

	Per cent
Isobutene polymer	40
Hydrogenated terpene resin, M. P. 115° C	25
Phenol modified terpene resin, M. P. approximately 130° C	25
Butoxy ethyl stearate	10

Example 10

	Per cent
Isobutene polymer	70
Hydrogenated terpene resin, M. P. 115° C	30

Example 11

Isobutene polymer	70
Hydrogenated terpene resin, M. P. 35° C	30

Plasticizers may be used in conjunction with the cohesive and adhesive agents and, in some cases (see Examples 6 and 7), the tack-promoting or adhesion-promoting agent may be a substance conventionally classified as a plasticizer. Plasticizers for the polybutene polymer include the following: alkyl esters of fatty acids, mineral oil, esters of dibasic acids, alkyl esters of abietic acid. Plasticizers for the vinyl polymer include: dibutoxy ethyl phthalate; triethylene glycol di-2-ethyl hexoate; di(para tertiary butyl phenyl) mono phenyl phosphate.

In order to apply the adhesive to the flexible transparent material, the components thereof, e. g., the total solids as illustrated by the above formulae, are dissolved in a suitable volatile solvent, for example benzol petroleum ether or hexane, in the proportion, for example, of 80% solvent and 20% solids. The resulting viscous solution is then coated on one side of the flexible material, preferably subsequent to the coating with a repellent, as hereinafter explained.

The apparatus and method of effecting the adhesive coating is not a part of the present application and need not be described in detail except to say that the coating with adhesive may be accomplished by means of a doctor blade fed with the viscous solution of adhesive from a hopper and maintained in suitable spaced relation to a roll. The process is continuous and the solvent,

after deposition of the adhesive solution, is completely removed during the process of manufacture, being evaporated by any suitable evaporation means. The solvent, therefore, merely acts as a vehicle to permit the application of the adhesive to the flexible transparent material.

The purpose of the repellent which is applied as a coating on the other side of the flexible transparent material is to avoid cementitious union of the adhesive with the opposite surface of the transparent material when the coated material is formed into a laminated roll and to permit the flexible transparent material to be readily unrolled as required. A repellent coating made in accordance with the present invention may comprise a surface-tension-lowering substance or detergent bonded to that surface of the transparent flexible material opposite the adhesive by means of a hydrophylic film-forming material. Among the surface-tension-lowering materials which may be employed are the salts of the alkyl sulphonamides of fatty acids identified by the trade name "Igepon," water-soluble soaps, e. g., alkali salts of fatty acids, salts of the acid esters of the higher alcohols, e. g., sodium lauryl sulfate, etc. Among the hydrophylic film-forming materials may be mentioned the wholly and partially hydrolyzed products of polyvinyl acetate, e. g., hydroxy polyvinyl acetate, and polyvinyl alcohol; gelatine, casein, methyl cellulose, etc. Hydrophylic film-forming substances and surface-tension-lowering substances may be employed, generically. The class or genus of these substances is per se well known and it is unnecessary to specifically list a large number of individual species.

Specific examples of preferred compositions of the repellent coating are as follows:

Example 12

	Per cent
Hydroxy polyvinyl acetate (Solvar)	64
Sodium oleate	32
Sodium hydroxide	4

Example 13

	Per cent
Hydroxy polyvinyl acetate (Solvar)	50
Igepon AP	50

Example 14

	Per cent
Methyl cellulose	66.6
Aerosol NAO (a dialkyl ester of a sulphonated dicarboxylic acid)	33.4

Example 15

	Per cent
Hydroxy polyvinyl acetate	66.6
Duponol ME (sodium lauryl sulphate)	33.4

Example 16

	Per cent
Casein	37.7
Sodium oleate	56.6
Borax	5.7
Dowicide B (preservative phenolic compound)	0.25

Example 17

	Per cent
Polyvinyl alcohol	50
Triethanolamine oleate	50

The invention is not limited in all of its forms to a hydrophilic film-forming substance and extends to the use of film-forming substances in general, provided they possess the necessary attributes of repellency. In general a film-forming substance having surface-tension lowering properties may be employed. For example, a hydrophobic film-forming substance illustrated by benzol soluble ethyl cellulose may be used, provided it is incorporated with a "slip" agent more accurately defined as a surface-tension-lowering agent. For example, a repellent coating may be formed by blending 66 parts by weight of benzol soluble ethyl cellulose with 34 parts by weight of triethanolamine oleate. The surface-tension-lowering agent may not only be blended physically with the film-forming agent, but may also be chemically combined therewith, as for example in a compound which is the oleic acid ester of hydroxy polyvinyl acetate and is known as Solvar. The mixed ester of cellulose with stearic and acetic acids may also be used. The important attribute of the repellent is that it should be both film-forming and repellent to the adhesive. In general, film-forming polymers containing hydroxyl groups capable of esterification with the higher fatty acids may, when so esterified, be used, the fatty acid radical contributing the necessary "slip" or repellent characteristics.

A preferred method of the application is as follows:

The solid material of the repellent coating as above set forth is dissolved in water to make a dilute solution, for example one having a concentration of total solids of about two or three per cent. A thin film of this solution is then coated on one side of the transparent flexible material by any suitable method, as, for example, by passing the transparent flexible material in contact with the surface of a roll which is continually wetted by said solution, and the coated film is then passed through a drier to completely eliminate the water. Where the repellent is insoluble in water, e. g., in the case of the oleic acid ester of hydroxy polyvinyl acetate, an appropriate organic solvent will of course be used. The flexible transparent material is thus provided with a repellent coating on one side and is then provided with an adhesive coating on the other side in the manner previously described.

It is to be noted that it is highly desirable to remove all solvents, including the last traces thereof, from both the adhesive and the repellent coatings prior to rolling up the product in the form of a roll because of the possibility that such solvent or traces thereof in one or the other of the coatings may, when the sheet is rolled up and stored, act upon the other coatings to the detriment thereof or to the detriment of both coatings and therefore the present invention includes the treatment of the product in such a way as to completely eliminate the solvents. For example, as above set forth, the sheet may be first provided with a repellent coating in which the repellent is a hydrophilic film-forming substance dissolved in water as a solvent and the sheet with its coating may then be dried by continuously passing it through a hot air drying chamber in which the temperature is maintained at, say, 280–300° F. at such speed and under such conditions as to insure the complete evaporation and removal of the water. Thereafter, the sheet coated on one side with the repellent is provided on the other side with a coating of adhesive which, for example, may comprise a polybutene dissolved in petroleum ether, and the sheet is then treated for the complete removal of the solvent, as for example by passing through a drying chamber in which the

temperature is maintained at, for example, 250-270° F.

However, it is desirable to guard against the possibility that the solvents may not be completely removed and it is therefore desirable that the solvent for the adhesive should be a non-solvent for the repellent and vice versa. Such is particularly true when the repellent is soluble or readily dispersible in water as a solvent, because in such case the repellent may be a hydrophilic substance, as above mentioned, for which the organic solvent, as for example petroleum ether, benzol and the like in which the adhesive is dissolved, is a non-solvent, and similarly water is, of course, a non-solvent for the substances preferably used in accordance with this invention as the adhesive.

Not only should the solvent for the adhesive coating be a non-solvent for the repellent, and the solvent for the repellent coating a non-solvent for the adhesive, but, in addition, as hereinbefore explained, the adhesive as a whole and the components thereof should not have any chemical or physical action on the repellent as a whole and the components thereof.

Moreover, the sheet, the adhesive, and the repellent, should be of such a nature that they are all mutually incompatible, at least to the extent that there shall be no physical or chemical interaction between these parts which would cause mutual impairment of the desirable properties thereof, and this is true, not only as to the adhesive, the sheet, and the repellent as a whole, but, of course, also as to the components thereof. For example, one of the preferred adhesives of the invention is a composition containing a polybutene polymer blended with a hydrogenated terpene resin polymer. One of the preferred species of the sheet is cellulose acetate and one of the preferred repellent compositions is a hydroxy vinyl acetate blended with sodium oleate and sodium hydroxide. The polybutene polymer and the hydrogenated terpene resin are not only incompatible with the cellulose acetate, but also with the constituents of the repellent, including the hydroxy vinyl acetate mentioned. Therefore, in practicing the invention and giving effect to the various equivalents thereof, this principle of mutual incompatibility is to be borne in mind.

I claim:

1. A composite permanently pressure-sealing non-reusable adhesive sheet structure adapted to be packaged in superimposed layer form, comprising a flexible backing, a coating of normally tacky pressure-sealing adhesive on one side of said backing having a permanent high sealing capacity to prevent removal once applied to a paper surface without partially destroying the paper surface and a coating of a material repellent to said adhesive on the opposite side of said backing, said adhesive and repellent being of a character to avoid cementitious union of the repellent and adhesive coatings when said coatings are maintained in direct contact over long periods of time in packaged form and thereby permit the sheets to be readily separated, said repellent comprising organic material having binding and detergent properties, said detergent being a member of a group consisting of soluble soaps, salts of the alkyl sulphonamides of fatty acids, alkali salts of the acid esters of the higher alcohols, dialkyl ester of sulfonated dicarboxylic acid, triethanolamine oleate, which material is incompatible with the ingredients of said adhesive coating.

2. A transparent composite permanently pressure-sealing non-reusable adhesive sheet structure adapted to be packaged in superimposed layer form, comprising a transparent flexible backing, a transparent coating of normally tacky pressure-sealing adhesive on one side of said backing having a permanent high sealing capacity to prevent removal once applied to a paper surface without partially destroying the paper surface and a transparent coating of a material repellent to said adhesive on the opposite side of said backing, said adhesive and repellent being of a character to avoid cementitious union of the repellent and adhesive coatings when said coatings are maintained in direct contact over long periods of time in packaged form and thereby permit the sheets to be readily separated, said repellent comprising organic material having binding and detergent properties, said detergent being a member of a group consisting of soluble soaps, salts of the alkyl sulphonamides of fatty acids, alkali salts of the acid esters of the higher alcohols, dialkyl ester of sulfonated dicarboxylic acid, triethanolamine oleate, which material is incompatible with the ingredients of said adhesive coating.

3. A composite pressure-sensitive adhesive sheet structure adapted to be packaged in superimposed layer form, comprising a flexible backing, a coating of normally tacky pressure-sensitive adhesive on one side of said backing and a coating of material repellent to said adhesive on the opposite side of said backing, said adhesive and repellent being of a character to avoid cementitious union of the repellent and adhesive coatings when said coatings are maintained in direct contact over long periods of time in packaged form and thereby permit the sheets to be readily separated, said repellent comprising organic material having binding and detergent properties, said detergent being a member of a group consisting of soluble soaps, salts of the alkyl sulphonamides of fatty acids, alkali salts of the acid esters of the higher alcohols, dialkyl ester of sulfonated dicarboxylic acid, triethanolamine oleate, which material is incompatible with the ingredients of said adhesive coating.

4. A composite pressure-sensitive adhesive sheet structure adapted to be packaged in superimposed layer form, comprising a transparent flexible backing, a transparent coating of normally tacky pressure-sensitive adhesive on one side of said backing and a transparent coating of material repellent to said adhesive on the opposite side of said backing, said adhesive and repellent being of a character to avoid cementitious union of the repellent and adhesive coatings when said coatings are maintained in direct contact over long periods of time in packaged form and thereby permit the sheets to be readily separated, said repellent comprising organic material having binding and detergent properties, said detergent being a member of a group consisting of soluble soaps, salts of the alkyl sulphonamides of fatty acids, alkali salts of the acid esters of the higher alcohols, dialkyl ester of sulfonated dicarboxylic acid, triethanolamine oleate, which material is incompatible with the ingredients of said adhesive coating.

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