March 31, 1970 E. C. AYRES 3,503,782

DIFFERENTIAL RELEASE PAPER

Filed May 29, 1967 2 Sheets-Sheet 1

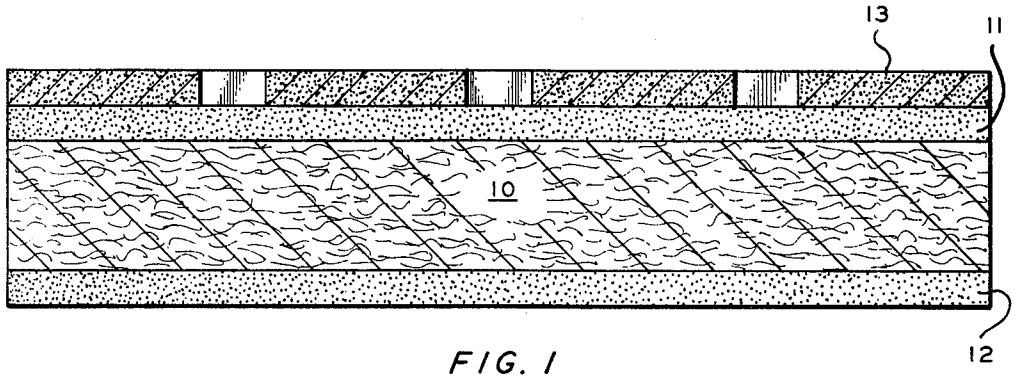

FIG. 1

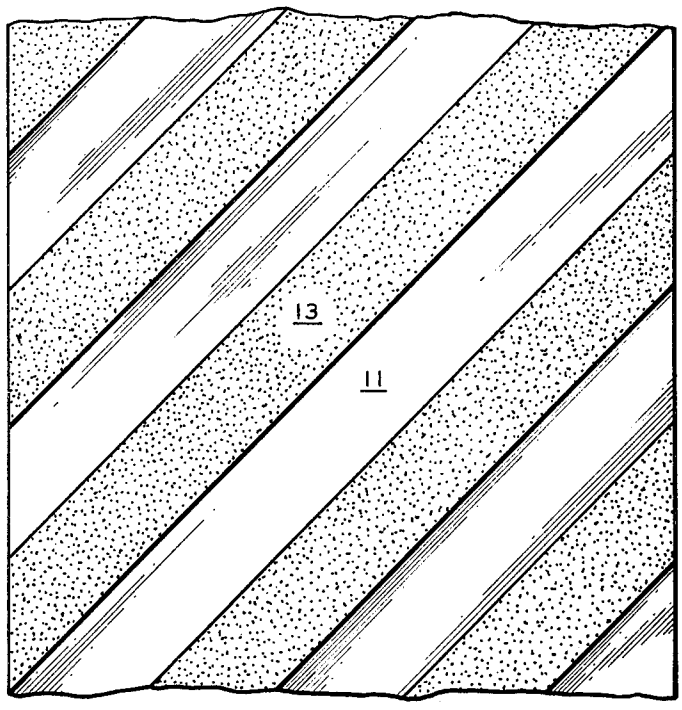

FIG. 2

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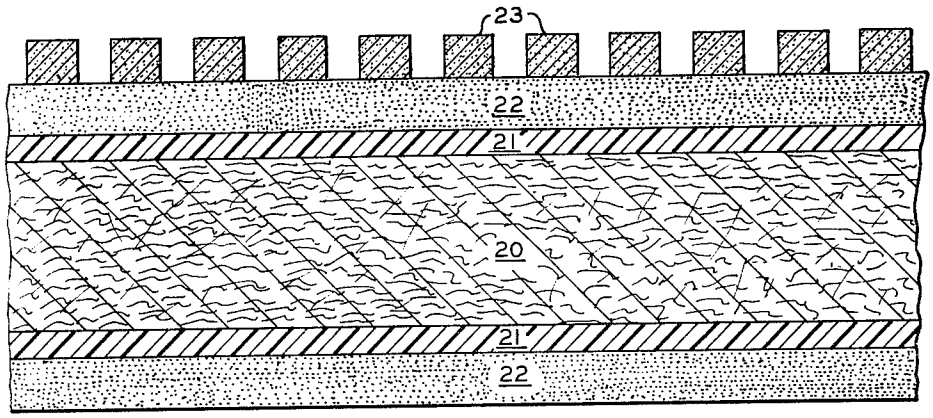

FIG. 3

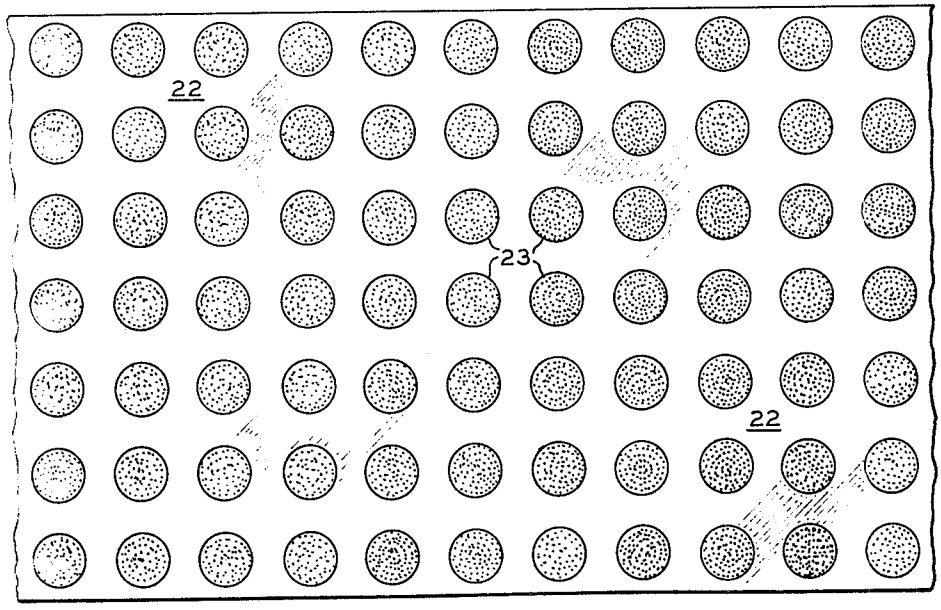

FIG. 4

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3,503,782

DIFFERENTIAL RELEASE PAPER

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Continuation-in-part of application Ser. No. 602,841, Dec. 19, 1966. This application May 29, 1967, Ser. No. 642,086

Int. Cl. D21h *1/10;* B44d *1/14*

U.S. Cl. 117—45 13 Claims

ABSTRACT OF THE DISCLOSURE

A differential release paper having an initial coating of a first release agent and a coating of second release agent applied over a portion of the initial coat; the release agents having different release characteristics.

This is a continuation-in-part of my copending application, Ser. No. 602,841, filed Dec. 19, 1966, now abandoned.

This invention relates to a method for applying a release agent to the surface of a paper substrate. In another aspect, it relates to an improved differential release paper.

Differential release papers will be defined in this application as those papers wherein the surfaces have nonsimilar release characteristics. Applying a release agent to part of an area refers to placing a release agent on only a portion of the surface, either in a particular pattern or not. A release agent will be defined as a material that promotes the release of an adhesive bonded thereto so as to not damage the adhesive qualities.

Prior art provides for altering the release strength of a surface coated with release agents by altering the characteristics of the release agent itself. Stated another way, the prior art teaches the application of the release agent over the entire surface and selection of a particular release agent to achieve a given release strength.

This invention provides for an improvement over the prior art in that this invention provides for the alteration of release strength by covering with a release agent only a part of a surface that previously has been completely covered with a different release agent. In other words, rather than selecting a release agent that corresponds to a given release strength, it is now possible to produce a surface of desired release strength by applying a release agent of greater release strength than desired only to a part of a surface that has been first completely coated with another release agent.

In one embodiment, the invention was used to create a differential release paper by coating both sides of a paper completely with a first release agent and then coating only a part of one side with a second release agent; the release agents having different release characteristics. Other embodiments of this invention include completely coating one side and then applying a release agent over only a part of the same side, and also completely coating both sides with a first release agent and applying a second release agent to only a part of both sides.

The functioning of a release agent will now be described. According to this invention, a release agent is applied to paper substrate. If there were no release agent applied to the paper, the paper would not pull free when bonded to an adhesive. If, however, a release agent has been first applied to the paper and then the release agent bonded to the adhesive, the paper and release agent will pull free from the adhesive without damaging the adhesive. Stated another way, the release agent protects the adhesive from coming in contact with the paper, and

thus prevents the paper from damaging the adhesive when pulled away.

In certain situations, it is desirable to produce a substrate that will release from one side at a greater or lesser strength than the other side. This can be accomplished by selecting release agents of different release strength for each side. According to this invention, however, a differential release strength phenomenon is effected by coating both sides with a release agent of equal release strength and then applying a second release agent of greater or lesser release strength to only a portion of one side. Thus, the release qualities of the side to which the second release agent is applied result from a combination of the release powers of both the first and second release agents. If the second release agent has a greater release strength than the first release agent, then the release strength of the combination of the first and second release agents is greater than the first release agent alone. Stated another way, the side coated in its entirety with the first release agent and then partially coated with the second release agent releases at greater strength than the side coated only with the first release agent. Thus, a differential release phenomenon has been effected. If the second release agent has a lesser release strength than the first agent, the side partially coated with the second release agent has a composite release strength less than the other side.

The invention resides in applying a release agent to only a part of a surface that has been first coated in its entirety with a release agent which has an inherent degree of release ability. In a preferred embodiment, the second coating is applied in the form of a pattern. It is, however, fully within the scope of this invention to apply the second coating of release agent in any manner that results in only partial coverage of the surafce.

Accordingly, it is an object of the invention to provide an improved differential release paper.

Another object of this invention is to provide an alteration in release strength by coating with a release agent only a part of a surface that has been previously covered completely with a release agent.

Another object of this invention is to provide a differential release paper by first coating both sides with a release agent and then coating only a part of one side with a release agent.

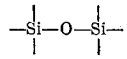
Other objects, advantages, and features of this invention will be readily apparent to those skilled in the art from the following description, drawing, and appended claims.

With reference to FIGURE 1, there is indicated a cross-sectional view of one embodiment of this invention. With reference to FIGURE 2, there is indicated a plan view of the same embodiment of the invention.

With more particular reference to FIGURE 1, there is indicated a paper substrate **10**. Specifically, paper coated on both sides with polyolefins is entirely satisfactory. Some polyolefins, such as polyethylene, have inherent degree of release ability. Paper is used in the practice of the invention because of the wide variety of applications in which it can be employed. It should be understood that the invention is not limited to any particular type of paper. The invention is applicable to any paper having sufficient tensile strength to be handled in conventional paper coating and treating apparatus. Thus, the invention is applicable to all types and weights of paper ranging from glassine to heavy paperboard, e.g., having weights in the range of from 25 to 150 pounds per ream.

With further reference to FIGURE 1, there is indicated a release agent coating **11** applied to the entirety of a first side. This coating can comprise a wide variety of release agents. Those materials comprising organo-

polysiloxanes (commonly called "silicones") are particularly desirable. Said organopolysiloxanes are also sometimes referred to as polymeric silicone resins, rubbers, or oils. These compositions are comprised essentially of silicon atoms connected to each other by oxygen atoms through silicon-oxygen linkages, e.g.,



(1)

The compositions used in the practice of the invention are preferably, but not necessarily, high molecular weight polymers and copolymers having molecular weights in the range of 5000 to 250,000. They should not have obtained such a degree of polymerization or condensation that they are no longer soluble in common hydrocarbon solvents, such as xylene, toluene, methyl ethyl ketone, and carbon tetrachloride. In general, any organic solvent having a boiling point equal to or less than that of xylene can be used in the compositions used in the practice of the invention. The solvent merely serves as a convenient vehicle or carrier for uniform application to the substrate. Thus, higher boiling point solvents can be used but require so much time for their removal that their use is not commercially economical. Various organopolysiloxanes are commercially available in organic solvents, in various percent solids concentration.

Generally speaking, organopolysiloxanes which can be used in the practice of the invention include those polymers wherein the recurring structural unit is



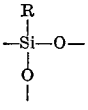
(2)

those polymers wherein the recurring structural unit is



(3)

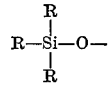
those polymers wherein the recurring structural unit is



(4)

and copolymers wherein the recurring structural units are (2) and (3) as above. In the above recurring structural units each R can be any suitable monovalent hydrocarbon radical such as aklyl, cycloalkyl, aryl, alkaryl, and aralkyl. Preferably, each R is selected from the group consisting of alkyl radicals containing from 1 to 6 carbon atoms, and phenyl. Compositions wherein each R is methly, ethyl, phenyl are presently more preferred.

Another type of structural unit which may be found in the above-described organopolysiloxanes in small amounts is



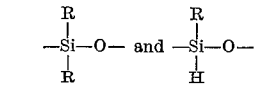
(5)

wherein R is as defined above. This structural unit is found as a terminal unit in a polymer chain because the R groups are not capable of further condensing or crosslinking.

Examination of the above structural units (2), (3), and (4) shows that in a polymer consisting essentially of recurring units of (2) or (4) the R/Si ratio (numerical ratio of the number of R groups to the number of Si atoms) will approach 2 when one does not consider the terminal units (5). It is obvious that in the high molecular weight polymers (about 5,000 to about 250,000 molecular weight) it is perfectly proper to not consider the few terminal groups which will be present. Similarly, in a polymer consisting essentially of recurring units of (3), the R/Si ratio will approach 1. It is also within the scope of the invention to mix and use physical mixtures of

said polymers consisting essentially of said recurring structural units (2), (3), and (4), and wherein the R/Si ratio is between about 1 and about 2. Thus, broadly speaking, the organopolysiloxanes which can be used in the practice of the invention are those having a R/Si ratio within the range of from about 1 to about 2.

However, the presently more preferred organopolysiloxanes for use in the practice of the invention are said copolymers consisting essentially of recurring structural units like (2) and (3) above, i.e.,



(6)

wherein each R is as defined above. Such copolymers can be prepared according to methods known to the art. For example, by hydrolyzing a mixture of desired amounts of dimethyldichlorosilane monomer and methylhydrogendichlorosilane comonomer,

$$[(CH_3)_2SiCl_2]_x \text{ and } [(CH_3HSiCl_2]_y \qquad (7)$$

where x and y are integers which represent the amount in mols of the respective monomers used in said mixture and which determine the R/Si ratio in the copolymer. A small amount of trimethylchlorosilane, $(CH_3)_3ClSi$, is added to supply the terminal $(CH_3)_3Si$— end groups. Other methods of preparing said copolymers are known to the art. For example, said copolymers can be formed by preparing cyclic tetramers of each monomer in dilute solution in suitable solvent and then causing rearrangement of the cyclic compounds in the absence of solvent.

Preferred copolymers are those where the R/Si ratio is within the range of from about 1.75 to less than 2, more preferably about 1.9 to less than 2, still more preferably about 1.95 to about 1.99. When neglecting the $(CH_3)_3Si$— terminal groups as discussed above, the relationship between x and y and the R/Si ratio can be illustrated by the following tabulation, Table I.

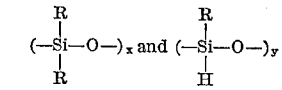
TABLE I

Mols of x	Mols of y	R/Si Ratio
100	0	2
99	1	1.99
95	5	1.95
75	25	1.75

It is obvious that the above relationships will not hold in low molecular weight copolymers because of the extra CH_3— group in the terminal group. However, in the high molecular weight copolymers used in the practice of the invention (about 5,000 to about 250,000 M.W.) the effect of said terminal groups can be disregarded.

The presently most preferred organopolysiloxane for use in the practice of the invention is a copolymer prepared, for example, by hydrolyzing a mixture such as (7) above wherein x is about 95 and y is about 5 to give a CH_3/Si ratio of about 1.95.

Since in the above illustrated monomers (7) each molecule of dimethyldichlorosilane monomer furnishes one structural unit (2) wherein R is CH_3—, and each molecule of methylhydrogendichlorosilane monomer furnishes one structural unit (3) wherein R is CH_3—, the preferred copolymers of the invention can be described as consisting essentially of the recurring structural units (2) and (3)



(8)

where R is as defined above, and x and y as are defined above and denote the relative numbers of said structural units in the copolymer and determine the R/Si ratio. For example, referring to Table I, when x=95 and y=5, the copolymer will contain 95 of the structural units (2) for each 5 of the structural units (3) and the R/Si ratio will be 1.95 when disregarding the terminal groups. Since

there will always be some of the structural unit (3) present in the copolymer, the R/Si ratio will approach 2 for decreasing values of y which are less than 1. However, when disregarding the terminal $(R)_3Si$— groups as discussed above, said ratio will always be less than 2.

The other above-described organopolysiloxanes can be prepared in a number of ways, all known in the art. For example, the preparation of methyl polysiloxane, also known as methyl silicone resins, is described in U.S. Patent 2,258,218. The preparation of ethyl polysiloxane resins, also known as ethyl silicone resins, is described in U.S. Patent 2,258,220. U.S. Patent 2,258,222 described still other types of silicone resins wherein one methyl radical in the structural units described above is replaced with an aryl group, such as a phenyl group. Other methods of preparing said organopolysiloxanes are described in U.S. Patent 2,494,920.

Filler materials in finely divided form, can be added to organopolysiloxanes to control the rheological properties and release characteristics of the agent. The filler materials can be either inorganic or organic, are chemically inert with respect to the organopolysiloxanes and substantially insoluble in the solvent used as the vehicle in applying the release agent.

Examples of inorganic fillers which can be employed include calcium carbonate, titanium dioxide, silica, alumina, mica, calcium silicate, zinc oxide, iron oxide and other polyvalent metal oxides. Examples of organic filler material which can be used include poly(vinyl chloride); polyesters, such as Mylar; polyamides, such as nylon; polycarbonates, such as Lexan; and other thermoplastic or thermosetting polymers or resins.

The particle size of the filler material is not critical over a wide range so long as the material is in a finely divided state, for example, materials having a particle size in the range of 0.1 to 250 microns, or greater, can be employed. It is important that the filler material be thoroughly mixed into a uniform suspension in the organopolysiloxane coating composition. The fillers are usually added in a filler to silicone weight ratio within the range of from 0.25:1 to 3:1, based on the silicone solids in the organopolysiloxane coating composition.

The above-described organopolysiloxanes in solution, and either filled or unfilled as described herein, are applied to the substrate surfaces in amounts, on a dry basis, within the range of from 0.03 to 0.4, preferably 0.06 to 0.25, pound per ream. Preferably, said organopolysiloxane is applied in two thin coats. However, it is within the scope of the invention to make the application in one coat. The amount and type of organopolysiloxane in each said coat on the same side or on opposite sides of the substrate can be the same or different.

The composition of the filled organopolysiloxane coating compositions which can be used in the practice of the invention can vary over a wide range, depending upon the properties desired. Usually the amounts of the components of said composition will be within the following ranges, in weight per cent: polymeric silicone solids, from about 2 to about 10; filler, from 0.5 to about 30; and solvent, from about 60 to 97.5. Said solvent can be any of the solvents normally used for preparing solutions of organopolysiloxanes as set forth above. When the filler is one of the above-described organic fillers, it is sometimes desirable that from about 4 to about 10 percent of said solvent be an aliphatic hydrocarbon containing from 5 to 9 carbon atoms per molecule, or mixtures thereof such as light naphthas and gasolines, to control the solubility of said filler in the overall solvent. Paraffinic and isoparaffinic hydrocarbons are preferred.

Prior to application of the organopolysiloxane coating composition, a small amount of a suitable catalyst or curing agent is added thereto. Suitable catalysts for this purpose include dibutyl tin di-2-ethyl hexanoate, dibutyl tin dilaurate, dibutyl tin diacetate, tributyl tin acetate, diethylene triamine, triethylene tetramine, various lead salts such as lead naphthenate and lead octoate, zinc octoate, zinc stearate, iron octoate, various organic peroxides such as benzoyl peroxide, and others. The amount of said curing agents or catalysts used is not critical and can be varied widely depending upon the curing temperature, the particular catalyst used, desired curing time, the particular silicone polymer, etc. Usually, the amount used will be from 1 to 10 weight percent of the silicone polymer.

Curing of the organopolysiloxane coating material can take place at room temperature depending upon the particular silicone material used and the particular curing agent or catalyst used in conjunction with the silicone material. However, for practical continuous operation the time required for curing at room temperature is too long. Most curing agents are capable of promoting relatively rapid curing at moderately elevated temperatures. This temperature at which relatively rapid curing takes place is sometimes referred to as the curing initiating temperature even though curing will take place at room temperature. For the preferred organopolysiloxanes described herein, this temperature is in the range of 180 to 250° F. Once curing has been initiated and maintained at an elevated temperature for a short period of time, the curing can be allowed to proceed by aging at reduced temperature, for example room temperature, to obtain a substantially dry film.

With additional reference to FIGURE 1, there is indicated a release agent coating **12** applied to an entirety of a second side of substrate **10**. All comments concerning release agent coating **11**, applied to the entirety of a first side, are equally applicable to release agent coating **12**, applied to the entirety of a second side. With further reference to FIGURE 1, there is indicated release agent coating **13** applied in a pattern. In this specific embodiment of the invention the pattern consists of a series of lines. It is fully within the scope of my invention, however, to alter the pattern to include a pattern composed of any geometrical unit, such as dots, squares, triangles, rectangles, and the like. It is also within the scope of this invention to apply release agent coating **13** in a non-pattern formation, such as random placement of the agent. It is then readily obvious that any application of release agent is satisfactory as long as only a part of the surface is covered.

FIGURE 3 and FIGURE 4 depict a substrate **20** having a polyolefin coating **21** on both sides. The polyolefin coating **21** is coated with a first release agent **22**. The top coating of release agent **22** is overcoated with a dot pattern of a second release agent **23** in this embodiment of this invention.

EXAMPLE

In one specific embodiment of this invention, a differential release substrate was produced and tested. Specifically, a substrate comprising paper with a .85 mil-thick polyethylene layer on both sides was coated, by use of a gravure roll, with a first unfilled organopolysiloxane release agent on both sides and cured. One side was then overcoated with a dot pattern of a second silicone release agent of an organopolysiloxane with a resin filler and dibutyl tin di-2-ethyl hexonate as a curing agent and cured. This embodiment is illustrated in FIGURE 3 and FIGURE 4. This second release agent had greater release characteristics than the release agent used for the initial coating.

A first sample was prepared with only the coating of first release agent as a control. A second sample, similar to the first, was prepared and an overcoat of the second release agent was applied in a dot pattern, the dots being about 1/32 of an inch apart. A third sample, similar to the first, was prepared and an overcoat of the second release agent was applied in dot pattern, the spacing between dots being less than that of the second samples. The samples were tested by stripping Johnson & Johnson Red Cross Waterproof Adhesive Tape from the sample

surface at a constant speed pull of 12 inches per minute. A Keil testing machine was employed in the testing. The average release values for the three samples are given below:

TABLE II

Sample No.:	Avr. release (grams/inch)
1 (control)	17
2	247
3	66

This data indicates the higher release characteristics obtained from the pattern coating. Also, comparison of the release values for samples 2 and 3 shows the effect of the pattern density or dot frequency on the release characteristics.

In this embodiment the second release agent possessed greater release characteristics than the first release agent. This resulted in the increased release characteristics shown in the data. If the second release agent had possessed a lower release characteristic than the first coating the result would have been a reduced release characteristic.

Reasonable modification and variation are within the scope of the invention which set forth a novel differential release paper.

What is claimed is:

1. A method of producing a surface having a desired release strength comprising the steps of uniformly applying a first release agent coating to one surface of a paper substrate so as to entirely cover said one surface; and applying a second release agent coating of a different release agent to only a part of said one surface.

2. The method of claim **1** wherein said second release agent coating is applied in the form of a pattern.

3. The method of claim **2** wherein the part of said surface to which the second release agent is applied comprises a dot pattern.

4. The method of claim **1** wherein each said release agent comprises a cured coating of an organopolysiloxane having an R/Si ratio within the range of about 1 to about 2, where R is a monovalent hydrocarbon radical.

5. The method of claim **4** wherein said monovalent hydrocarbon radical comprises CH_3—.

6. The method of claim **1** wherein a third release agent coating is applied to a second surface of said paper and the release strength of said third coating is different from the release strength of the combined coating on said one surface.

7. The method of claim **6** wherein said first and third release agent coatings are of the same release agent.

8. An article of manufacture of differential release characteristics comprising a paper substrate; a first release agent coating totally applied to a first side of said substrate to form a first surface; a second release agent coating totally applied to a second side of said substrate to form a second surface; and a third release agent coating applied to a part of said first surface.

9. The article of manufacture of claim **8** wherein said paper substrate comprises a paper coated on both sides with polyethylene; and wherein the part of the surface to which the third release agent is applied comprises a dot pattern.

10. The article of manufacture of claim **8** wherein said third release agent coating is applied in the form of a pattern.

11. The article of manufacture of claim **8** wherein said first and third coatings are of the same release agent.

12. The article of manufacture of claim **8** wherein each said release agent comprises a cured coating of an organopolysiloxane having an R/Si ratio within the range of about 1 to about 2, where R is a monovalent hydrocarbon radical.

13. The article of manufacture of claim **8** wherein said monovalent hydrocarbon radical comprises CH_3—.

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ALFRED L. LEAVITT, Primary Examiner

M. F. ESPOSITO, Assistant Examiner

U.S. Cl. X.R.

117—76; 156—289

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,503,782 Dated March 31, 1970

Inventor(s) Elwyn C. Ayres

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 8, line 30, delete the numeral "8" and insert therefor the numeral -- 12 --.

SIGNED AND
SEALED
AUG 11 1970

(SEAL)
Attest:

Edward M. Fletcher, Jr.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents

FORM PO-1050 (10-69)

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