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## SILOXANE PAPER RELEASE COATINGS

Peter S. Thomas, Livonia, Mich., and Thomas F. Maguire, Troy, N.Y., assignors to General Electric Company, a corporation of New York  
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### ABSTRACT OF THE DISCLOSURE

A paper release coating composition contains a silanol terminated gum, a silane containing 3 or 4 acetoxy groups, a metal salt and an organic solvent. A surface of a sheet of paper is coated with the composition, the solvent is removed and the silanol is crosslinked by reaction with the polyacetoxy silane in the presence of moisture at an elevated temperature. The coated paper produced is useful as a backing sheet for surgical adhesive tape.

This invention is concerned with rendering cellulosic materials non-adherent to various organic solids. More particularly, the invention is concerned with a process for rendering paper or paperboard non-adherent to normally adherent materials such as, for example, asphalts, bitumen, tars, waxes, paraffin solids, flour-containing pastes, and frozen foods, and other high molecular weight polymers and to the papers so treated. The process comprises treating the cellulosic material with a mixture of ingredients comprising (1) a linear polydimethylsiloxane containing terminal silicon-bonded hydroxyl groups, (2) a silane containing at least three acyloxy groups, and (3) an organometallic salt.

Cellulosic fibers in the form of cellulosic papers and paperboard are used extensively as confining and shipping means for various highly adhesive materials, including such organic compositions as asphalt or pitch, tar, various unvulcanized rubbers, particularly synthetic rubbers, other high molecular weight organic polymers used as adhesives, etc. For optimum use of the cellulosic containers, it is essential that they be capable of being readily separated or stripped from the cargo which they contain or from other bodies which carry the highly adhesive materials. Thus, in the transportation and shipment of asphalt used for roofing purposes, the asphalt is generally poured while still hot into a container, such as a carton, bag, or drum whose sides are cellulosic in nature. After cooling, the asphalt becomes quite hard and can be readily transported with little difficulty. At the point of use, it is essential that the paper be capable of being readily stripped from the asphalt so as to permit easy access to the asphalt without adherence of extraneous portions of the paper or fibers which might undesirably affect the constitution of the asphalt.

Various treatments have been accorded to these types of papers, often referred to as "anti-blocking paper" or "release paper." One method for treating the paper to render it anti-blocking comprises treating the paper in a three-coating operation with (1) finely divided clay in casein, (2) finely divided clay, and (3) polyvinylacetate. Such paper is released by fracture of the clay coating, but the polyvinylacetate remains on the adhesive material. Another method commonly employed in the art involves applying several thicknesses of polyethylene to the paper, usually by treating the latter with solutions of the polyethylene. A still further method for treating cellulosic material to render it non-adherent, particularly to asphalt, and to permit it to be readily removed from direct contact with the latter, involves depositing a double coating on the cellulosic materials, the first

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coating being of clay, and the second being of methylcellulose and starch.

The use of methylhydrogenpolysiloxanes in combination with water-soluble cellulose ethers for the purpose of treating anti-blocking paper to render it less adherent to ordinary adhesive organic compositions has previously been described. Although such combinations of ingredients are ordinarily helpful in reducing the adhesive properties of the paper, much is left to be desired from such treatment of the paper. Often, the release properties are unreliable and the release characteristics are not uniform throughout the surface of the paper. In addition, it is essential, in order to obtain optimum release properties, that the treated paper be aged for extended periods of time, e.g., by storage, before it is useful for release purposes. This storage is necessary because accelerated aging by high-temperature treatment is not usually available commercially in paper-treating establishments. Furthermore, paper such as parchment paper, cannot be heated above 125° C. without deleteriously affecting the paper. Moreover, after treatment of the paper with methylhydrogenpolysiloxane, the adhesive characteristics (i.e., the release properties) tend to decrease with time so that after long-term storage, such treated paper no longer shows adhesive characteristics.

In addition to the difficulties described above, particularly when using methylpolysiloxanes for anti-adhesion (adhesive) purposes, and even when using the more currently employed methylhydrogenpolysiloxanes for this purpose, it has been found that, although release properties are improved, nevertheless, there is an undesirable tendency of the silicone in the adhesive paper to migrate to the surface of the paper, thereby coming in contact with the material which it is desired to release. Often the adhesive paper is in contact with the compositions which are destined to be used for adhesion applications, and the tack or adhesion is undesirably reduced as a result of this migration of the organopolysiloxane from the treated release paper to the adhesive.

An additional problem is presented when cellulosic fiber sheets are coated with polysiloxanes for the purpose of forming "release paper" to be used in conjunction with adhesives tapes and labels. Many of the coatings of the prior art have a tendency to migrate from the treated surface to an adjacent uncoated side, making that surface unprintable. Additionally, such coatings require a high temperature for cure, e.g., 250° F.-300° F., and if cured at temperatures below 250° F., may not only migrate, but can cause blocking or sticking together of the adjacent layers when the coated paper is rolled up. Migration also causes a loss of adhesion in pressure-sensitive adhesive tapes and labels which come into contact with the coated paper. One method employed to achieve the desirable properties without high temperature curing was the use of methyltrichlorosilane  $[(CH_3)_3SiCl_3]$  as a low temperature curing agent for the polysiloxanes in the treating solution. However, the by-product, hydrogen chloride, generated by the curing reaction using the methyltrichlorosilane contaminated and corroded the coating equipment so that the practice of using this material as a curing agent was abandoned.

In accordance with our invention, a method has been found for providing a non-blocking siloxane release coating on a cellulosic fiber sheet which can be cured at low temperature to produce a non-migrating coating, while still providing the desired release properties.

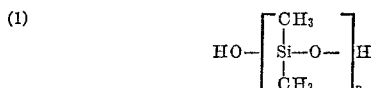
It is, therefore, one object of this invention to provide a method for rendering cellulosic fiber sheet materials non-adherent to normally adhering substances by treating with a coating material which can be cured at low temperatures.

It is a further object of this invention to provide a method for rendering cellulosic fibrous sheet materials non-adherent to normally adhering substances by treatment with a solution containing a low temperature curing, non-migrating, non-smearing polysiloxane composition.

It is a still further object to produce a cellulosic fibrous sheet material treated in accordance with this invention.

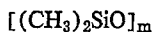
Briefly, the compositions which are used to obviate the above-mentioned problems and provide a release coating which is cured at low temperatures comprise solvent solutions of (1) a linear polydimethylsiloxane gum having terminal silicon-bonded hydroxyl groups, (2) a silane having at least three acyloxy substituents, e.g., methyltri-*acetoxy*silane, and (3) an organometallic salt, such as dibutyl tin dilaurate.

The polydimethylsiloxanes employed in the practice of the present invention are those having the general formula,



where  $n$  is an integer equal to at least 4500, for example, 4500 to 7500. These polydimethylsiloxanes, containing terminal silicon-bonded hydroxyl groups are soluble in organic solvents such as benzene, toluene, xylene, trichloroethylene, etc. The minimum average number of dimethylsiloxyl units is required to provide a penetration level for the gum sufficient to give the necessary properties to the ultimate release coating. The maximum penetration which can be used is about 1000, a penetration corresponding to a dimethylpolysiloxane gum having a molecular weight of about 350,000 and a viscosity of about 10,000,000 centistokes. The penetration is measured in 0.1 mm./min. using A.S.T.M. Standard Test No. D-217-60 T with a modified plunger or foot. The plunger or foot utilized to measure the penetration of the organopolysiloxane gums described in this application consists of a cylinder  $\frac{1}{4}$ " in diameter and  $\frac{3}{16}$ " long formed of brass and attached to a shaft of steel having a diameter of  $\frac{1}{8}$ " and a length of approximately  $5\frac{1}{8}$ ". This plunger weighs approximately 9.1 g. For purposes of the test, a 100 g. load is placed on the shaft. Correspondingly, a dimethylpolysiloxane gum with a molecular weight of about 550,000 has a viscosity in the range of 50,000,000 centistokes and a penetration of approximately 100. The lower penetration gums provide coatings which are smear-resistant, and thus are the most desirable for purposes of release. The preferred gums are those having the lowest penetrations, and thus the highest molecular weights.

These polydimethylsiloxanes can be prepared by any one of several well known methods. Thus, the high viscosity polydimethylsiloxanes can be obtained by condensing the hydrolysis product of dimethyldichlorosilane with either acidic or alkaline catalysts such as hydrochloric acid, sulfuric acid, potassium hydroxide, etc. Alternatively, one can heat cyclic polymers of the formula



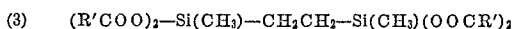
where  $m$  is an integer equal to from 3 to 6, for instance, octamethylcyclotetrasiloxane, with an alkaline catalyst such as potassium hydroxide in an amount of from 0.001 to 0.1% based on the weight of the octamethylcyclotetrasiloxane, at temperatures of from 125° C. to 175° C. for times ranging from about 15 minutes to 2 hours or more and thereafter, if desired, removing the alkaline catalyst. By treating the material with water and heating, terminal hydroxyl groups will be formed on the polydimethylsiloxane. This yields a polydimethylsiloxane of Formula 1 having a viscosity of from about 10,000,000 to 50,000,000 or more centipoises when measured at 25° C.

The organosilicon compound which is used to cure the silanol chain-stopped dimethylpolysiloxane gum is selected from compounds having the formula,



where R is a monovalent hydrocarbon radical free of aliphatic unsaturation, R' is an alkyl group having from 1 to 4 carbon atoms, and  $a$  is an integer from 0 to 1. More specifically, the R substituent can be an alkyl group such as methyl, ethyl, propyl, etc.; a cycloalkyl group such as cyclopentyl, cyclohexyl, etc.; an aryl group such as phenyl, naphthyl, biphenyl, tolyl, xylyl, ethylphenyl, etc.; an aralkyl group such as benzyl, phenylethyl, etc. Additionally, R can be a monovalent hydrocarbon radical substituted with groups such as cyano, carbalkoxy, and halogen substituents, e.g., beta-cyanoethyl, gamma-cyanopropyl, beta-carboxyethyl, beta-carbomethoxyethyl, gamma-hydroxypropyl, chloromethyl, dibromophenyl, etc. The R' substituent can be an alkyl group having from 1 to 4 carbon atoms such as methyl, ethyl, propyl, isopropyl, butyl, isobutyl, and *t*-butyl.

In addition to the acyloxy substituted silanes described above, cyclic siloxane compounds such as those having the formula,  $[(\text{R}'\text{COO})(\text{CH}_2)_b\text{SiO}]_b$ , where R' is as described above and  $b$  is an integer from 3 to 6, can be used. Further acyloxy substituted silylmethylene compounds such as those having the formula,



where R' is as defined above, will cure the silanol-terminated dimethylpolysiloxane gum. However, the results obtained with the acyloxy-substituted silylmethylenes are less satisfactory than those obtained using either the tri- or tetra-substituted silane or the acyloxy-substituted cyclic siloxane. The restriction that the R' substituent be an alkyl group of less than four carbon atoms is necessary because the acids formed as a by-product in the reaction are not easily removed from the reaction mixture if they contain more than five carbon atoms.

An excess of the acyloxy-substituted silane, with relation to the silanol chain-stopped gum, is always necessary. To provide this excess, the ratio of acyloxy substituted silane having the Formula 2 to the dimethylpolysiloxane gum containing silanol terminals should be in the range of from 0.5 to 1.5 weight percent of the silane based on the silanol chain-stopped gum. The preferred range of silane is from 0.75 to 1.25 weight percent. If less than 0.5 weight percent of the acyloxy-substituted silane is present, the result is an insufficiently cured material. If the level of the acyloxy-substituted silane is raised beyond 1.5%, the finally cured coating does not possess the desired release properties.

Various organometallic salts can be used as catalysts with the silanol gum-acyloxy substituted silane mixture. In general, these catalysts comprise the organometal salts of fatty acids. Exemplary of such salts are dibutyl tin dilaurate, zinc octoate, stannous octoate, dibutyl tin dioctoate, etc. Based on the silanol chain-stopped gum, there should be from 0.3% to 1.2%, as metal, of the catalyst. Below the level of 0.3% catalyst, sufficiently rapid cure at low temperatures is not achieved; if more than 1.2% of the cure-promoting catalyst is present, an undesirable film of the salt remains on the surface of the polysiloxane coating.

The polysiloxane coating is applied to the paper through the use of a solvent solution of the various materials. Stability of the solution, with respect to shelf life, depends upon the concentration of organosilicon materials in the solution and whether both the silanol chain-stopped dimethylpolysiloxane gum and the acyloxy-substituted silane are present in the solution during storage. When both the gum and the acyloxy-substituted silane are present in the same solution, the maximum concentration to provide a reasonable shelf life stability is approximately 10% solids. With 10% or less solids, a shelf life in the range of three months may be achieved. It is uneconomical to use the solution below a concentration of approximately 1%. If two solvent solutions are provided, i.e., one solvent solution containing the silanol chain-stopped dimethylpolysiloxane gum and one solution containing the

acyloxy-substituted silane, no shelf life problems are presented even when the concentrations of each of the materials in its respective solution is 30%. Here, obviously, the two solutions are mixed at the point of use so that shelf life is no longer a problem.

Thus, within the limits stated above, the coating solutions of the present invention can have an overall composition, by weight, as follows:

|                                                                       | Parts                   |
|-----------------------------------------------------------------------|-------------------------|
| (1) Dimethylpolysiloxane gum containing silanol chain terminals ----- | 1-30                    |
| (2) Acyloxy-substituted silane -----                                  | 0.005-0.45              |
| (3) Organometal salts of fatty acids -----                            | <sup>1</sup> 0.003-0.36 |
| (4) Solvent -----                                                     | 70-99                   |
| <sup>1</sup> As metal.                                                |                         |

A preferred range of substituents for the composition is as follows:

|                                                                       | Parts                   |
|-----------------------------------------------------------------------|-------------------------|
| (1) Dimethylpolysiloxane gum containing silanol chain terminals ----- | 1-30                    |
| (2) Acyloxy-substituted silane -----                                  | 0.008-0.375             |
| (3) Organometal salts of fatty acids -----                            | <sup>1</sup> 0.003-0.36 |
| (4) Solvent -----                                                     | 70-99                   |
| <sup>1</sup> As metal.                                                |                         |

A wide variety of solvents can be used for the coating solution. Particularly, the solvents can be aromatics such as benzene, toluene, and xylene. Additionally, solvents such as tetrahydrofuran, esters such as ethyl acetate, ketones such as methyl ethyl ketone, and substituted aromatic compounds such as toluene and chlorobenzene may be utilized. Solvents except for those just mentioned, while they may dissolve the various reactants, present shelf life problems in addition to those mentioned with relation to solution concentration. The order of addition of the various reactants to the solvent solution is immaterial.

As was previously described, the purpose of the present invention is to provide a solution which allows a release coating to be placed on paper without the necessity for a high temperature cure. Moisture, as from the air, will initiate curing of the material of the present invention, even at room temperature, but about 20 hours is required to complete the cure in the absence of a catalyst. When the cure-promoting catalyst is present in the solution, at temperatures of from 150° to 200° F., the various coatings may be cured in approximately 30 seconds. If the reaction temperature is lowered to 100° F., the cure will require approximately 1 minute. When the paper is coated in high speed paper coating machinery, a cure time of about 1 minute is the longest which may be tolerated, so that 100° F. is the lowest practical curing temperature. However, of course, if high speed paper coating equipment is not used, and it is only desired to provide a release coating on paper using a material which may be cured at a low temperature, the material of the present invention can easily be used with curing temperatures below 100° F. or without a catalyst.

The coating of the present invention is normally used on glassine paper or on clay coated paper. For practical release applications, there should be a uniform coating of the cured dimethylpolysiloxane gum in an amount of approximately ½ pound per 3,000 square feet. To make sure that the entire paper is coated, up to 1 pound of dimethylpolysiloxane gum can be employed per 3000 square feet; greater amounts of gum being uneconomical. A release coating which is workable, however, is produced with 0.2 pound dimethylpolysiloxane gum per 3000 square feet provided there is uniform coverage.

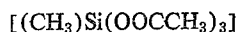
Following treatment of the cellulosic material with the solution of the present invention, the cellulosic material is advantageously dried by passing the treated paper over heated rolls maintained at temperatures of about 100 to 200° F. for up to one minute. The use of circulating hot air at similar temperatures may also be used for

times of from 15 seconds to one minute to effect curing of the treated paper. This drying step will bring out the optimum release properties of the paper without further heat treatment, and such optimum release properties are immediately available without requiring aging or storage of the treated paper.

The following examples are illustrative of the use of the process of the present invention and should not be considered as limiting in any way its full scope, as covered by the appended claims.

#### Example 1

A treating bath was prepared containing a 10% solution, in toluene, of a silanol chain-terminated dimethylpolysiloxane gum, methyltriacetoxysilane



in the amount of 1% based on the dimethylpolysiloxane gum and a solution of dibutyl tin dilaurate and xylene containing 6% tin, in an amount of 10% based on the dimethylpolysiloxane gum. The polysiloxane utilized for this treating bath had the same properties as the gum described in Example 1. The bath was applied to a clay-coated paper by standard metering techniques to provide a coating of one pound of gum per 3000 square feet of paper. The paper was then exposed to the air at room temperature and subsequently heated for 1 minute at 150° F. The paper-coated as just described was found to have release properties normally found in coatings cured at higher temperatures.

The release-coated paper was tested using Johnson and Johnson Surgical Tape and found to have an adhesion of 5-10 g./in. width. There was no evidence of migration when the tapes were subjected to the subsequent adhesion tests prescribed by the proposed TAPPI procedure. The test involves placing the tape which has been removed from the organopolysiloxane-coated paper on a clean 302 stainless steel panel having a 12 to 16 micro-inch ground finish. The tape is rolled with a 4.5 pound roller once in each direction and is then allowed to remain for 30 minutes at 73° F. and 50% relative humidity. The migration is determined by pulling the tape from the stainless steel panel and comparing the adhesion with that of tape which has not previously been applied to an organopolysiloxane-coated paper. The adhesion obtained for the paper was the same when it was tested immediately after curing, after aging for 1 month, and after aging for 2 months.

#### CONTROL EXAMPLE

A 10% solution of a silanol-stopped dimethylpolysiloxane gum, in toluene, and 1%, based on the siloxane of methyltriacetoxysilane  $[(CH_3)_2Si(OOCCH_3)_3]$  were mixed together. The polysiloxane had a molecular weight of about 500,000, a viscosity of  $35 \times 10^6$  centistokes, and a penetration of 150. A glassine paper was coated with the mixture using standard metering techniques to provide one pound of gum per 3000 square feet of paper. The paper sheet was exposed to air at room temperature for a period of about 20 hours. Approximately 10 minutes after application of the polysiloxane solution, the paper was tested and found to be non-blocking. However, release results were not optimum in that excessive migration was observed. There was a slight loss of tape adhesion indicating that, at this point, the coating was not completely cured. A portion of the paper was again tested approximately 20 hours after application of the treating solution. Following this longer period, the dimethylpolysiloxane coating was found to be completely cured.

#### Example 2

A coating bath was prepared by mixing a 10% solution, in toluene, of a silanol chain-terminated dimethylpolysiloxane gum, and methyltriacetoxysilane in an

amount of 1% based on the dimethylpolysiloxane gum, and a solution of dibutyl tin dilaurate in xylene containing 6% tin, in an amount of 10% based on the gum. The dimethylpolysiloxane gum had a molecular weight of approximately 425,000, a viscosity of about  $18 \times 10^6$  centistokes, and a penetration of 675. Glassine paper was coated utilizing standard metering techniques to provide a coating of one pound of gum per 3000 square feet of paper. The paper was exposed to the air at room temperature and then cured for 1 minute at 150° F. Immediately after completion of the cure, the paper was tested for release using Johnson and Johnson Surgical Tape and the adhesion was observed to be 5-10 g./in. width. Following 2 months aging, the adhesion had not changed substantially.

It is apparent from this disclosure that a practical method of treating cellulosic fibrous sheets at substantially reduced temperatures, including room temperature, to provide a release coating, which is non-blocking and non-migratory, has been provided. The amount of silanol-terminated dimethylpolysiloxane, acyloxy-substituted silane, and organometal salt catalyst can be varied within wide limits as previously disclosed. The materials and process described are equally applicable to one-step coating processes and to continuous processes for providing release coatings on cellulosic fibrous materials. Standard paper making or paper converting equipment can be readily employed in connection with the treating operations and no precautions need be taken for any toxic materials which may be contained in the solutions, other than those normally observed for the particular organic solvents.

The cellulosic materials treated as described above, have a wide range of usefulness. Thus, asphalt or high molecular weight organic polymers, such as various synthetic rubbers, can be poured hot into any containers fashioned from the treated paper or paperboard, and after cooling it will be found that the solidified asphalt or polymer is readily and cleanly separated from the container wall.

Further, the invention permits paper treated in accordance with this process to be substituted for various fabrics which heretofore have been used in contact with the adhesive surfaces of materials such as electrician's pressure-sensitive tape, adhesive tape used for surgical purposes, and regenerated cellulose tape carrying a permanent adhesive upon one surface. Vulcanized or unvulcanized sheets or rubber can be prevented from adhering despite the fact that these sheets of rubber may be quite sticky and cohesive when in direct contact with each other. Paper treated in accordance with the instant invention is also useful in lining various boxes of partially pre-baked goods such as buns, rolls, and the like, and advantage can be taken of the outstanding release properties at elevated temperatures by completing the baking cycle

in the original container in which the baked goods are purchased.

What is claimed as new and desired to be secured by Letters Patent of the United States is:

1. A method for rendering cellulosic fibrous sheet material non-adherent to surfaces which normally adhere thereto, comprising treating the sheet material with a bath consisting essentially of, by weight, the following ingredients:

- (1) from 1 to 30 parts of a linear dimethylpolysiloxane gum containing terminal silicon-bonded hydroxyl groups and having a viscosity of at least 10,000,000 centistokes at 25° C.,
  - (2) from 0.005 to 0.45 part of a silane having the formula  $\text{RaSi}(\text{OOCR}')_{4-a}$  where R is a monovalent hydrocarbon radical free of aliphatic unsaturation, R' is a monovalent alkyl radical having from 1 to 4 carbon atoms, and a is 1,
  - (3) from 0.003 to 0.36 part, as metal, of an organometal salt, and
  - (4) from 70 to 99 parts of an organic solvent, and thereafter heating the cellulosic fibrous base to at least 100° F. to effect a cure and remove the solvent.
2. The method of claim 1 wherein the silane is methyltriacetoxysilane.
3. The method of claim 1 wherein the silane is present in an amount of from 0.008 to 0.375 part.
4. The method of claim 1 wherein the organometallic salt is dibutyl tin dilaurate.
5. A method for rendering cellulosic fibrous sheet material non-adherent to surfaces which normally adhere thereto, comprising a treating the sheet material with a bath consisting essentially of, by weight, the following ingredients:
- (1) from 1 to 30 parts of a linear polydimethylsiloxane gum containing at least one terminal silicon-bonded hydroxyl group and having a viscosity of at least 10,000,000 centistokes at 25° C.,
  - (2) from 0.005 to 0.45 part methyltriacetoxysilane,
  - (3) from 0.003 to 0.36 part, as tin, dibutyl tin dilaurate, and,
  - (4) from 70 to 99 parts toluene, and thereafter heating the cellulosic fibrous base to at least 100° F. to effect a cure and remove the solvent.

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WILLIAM D. MARTIN, *Primary Examiner.*