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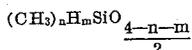
METHOD OF RENDERING CELLULOSIC MATERIAL NON-ADHERENT AND ARTICLE PRODUCED THEREBY

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4 Claims. (Cl. 117-143)

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 instance, asphalts, bitumen, tars, waxes, paraffin solids, flour-containing pastes and frozen foodstuffs, and other high molecular weight polymers, which process comprises treating the said cellulosic material with an aqueous emulsion containing as essential ingredients (1) a linear polydimethylsiloxane containing terminal silicon-bonded hydroxy groups, (2) a small amount of a methyl hydrogen polysiloxane having the formula



where n has an average value of from 1.0 to 1.5, m has an average value of from 0.75 to 1.25, and the total of $m+n$ is from 2.0 to 2.25, inclusive, and (3) a metallic salt selected from the class consisting of dibutyl tin dilaurate and dibutyl tin diacetate.

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 these cellulosic containers, it is essential that they be capable of being readily separated or stripped from the cargo contained therein. 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 its destination of use, it is essential that this paper, in whatever form, be capable of being readily stripped from the asphalt so as to permit easy access to the latter without any extraneous portions of the paper or fibers thereof adhering to the asphalt so as to undesirably affect the constitution of the asphalt.

Various treatments have been accorded these types of papers which are 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-coat operation with (1) finely divided clay and casein, (2) finely divided clay, and (3) polyvinyl acetate. Such paper provides release by fracture of the clay coating, but the polyvinyl acetate 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 of cellulosic material, the first

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coating being of clay and the second coating being of methyl cellulose and starch.

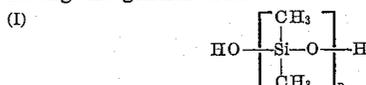
However, all the foregoing methods have been exceedingly expensive and in many respects have not been too satisfactory, since too often it has been found that these adhesive materials, particularly asphalt, which apparently has a high affinity for cellulosic fibers, stick to the anti-blocking paper so that great difficulty is encountered in attempting to separate the latter from the asphalt.

U.S. Patent 2,588,367 describes the use of methyl hydrogen polysiloxanes in combination with water-soluble cellulose ethers for the purpose of treating anti-blocking paper to render it less adherent to ordinarily adhesive organic compositions. Although such combinations of ingredients are ordinarily helpful in reducing the adhesive properties of the paper, nevertheless 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 that, in order to obtain optimum release properties, the treated paper be aged for extended periods of time, e.g., by storage before it is useful for release purposes; this 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 paper with the methyl hydrogen polysiloxane, 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 methyl hydrogen polysiloxanes for this purpose, it has been found that although release properties are improved, nevertheless there is an undesirable tendency of the organopolysiloxane 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 compositions which are destined to be used for adhesion applications, and the tack or the adhesion is undesirably reduced as a result of this migration of the organopolysiloxane from the treated release paper to the adhesive.

Unexpectedly, I have discovered that a certain mixture of ingredients can be used to treat release paper, and paper treated in this manner obviates the various difficulties recited above. What is even more important, release paper treated with these compositions shows no evidence of migration of the organopolysiloxane therein to the surface undesirably to contaminate the material with which the release paper may come in contact. The compositions which I have found to be so eminently suitable in the practice of the present invention comprise an aqueous emulsion composed of (1) a linear polydimethylsiloxane having terminal silicon-bonded hydroxyl groups, (2) a methyl hydrogen polysiloxane, and (3) a small amount of two tin salts, either alone or together, selected from the class consisting of dibutyl tin dilaurate and dibutyl tin diacetate.

The hydroxy chain-stopped polydimethylsiloxanes employed in the practice of the present invention are those having the general formula



where n is an integer greater than 1, for instance, from 25 to 100,000. These polydimethylsiloxanes containing

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terminal silicon-bonded hydroxyl groups (hereinafter referred to as "polydimethylsiloxane") are soluble in organic solvents such as xylene, toluene, trichloroethylene, etc., and are preferably of a fluid nature which may range in viscosity from highly fluid materials to difficultly flowable compositions; the viscosities of such polydimethylsiloxanes may range from about 50 to 2,000,000 centipoises when measured at 25° C.

These polydimethylsiloxanes may be prepared by any one of several well-known methods. When making the highly viscous polydimethylsiloxanes, such compositions may be obtained by hydrolyzing dimethyldichlorosilane with water and thereafter condensing the hydrolysis product with either acidic or alkaline catalysts such as hydrochloric acid, sulfuric acid, potassium hydroxide, etc. Alternatively, one may heat cyclic polymers of the formula



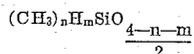
where m is an integer equal to from 3 to 6, for instance, octamethylcyclotetrasiloxane, with an alkaline catalyst such as potassium hydroxide, cesium hydroxide, etc. (in an amount equal, by weight, to from about 0.001 to 0.1% based on the weight of the octamethylcyclotetrasiloxane) at temperatures of from 125° to 175° C. for times ranging from about 15 minutes to 2 hours or more, and thereafter, if desired, removing or neutralizing the alkaline catalyst to yield a polydimethylsiloxane of Formula I having a viscosity of from about 700,000 to 2,000,000 centipoises or more when measured at 25° C.

When lower viscosity polydimethylsiloxanes containing terminal silicon-bonded hydroxyl groups are desired, one can treat the high molecular weight products obtained above with water to reduce the viscosity of the polymer to within the range of from about 50 to 100,000 centipoises at 25° C. This can be accomplished by blowing steam across the surface of the high molecular weight product or through the polymer for a sufficient time to give the lower viscosity material having the desired silanol content. Such compositions and various methods for preparing the same are more particularly described in U.S. Patents 2,607,792 and 2,779,776. The use of steam in this fashion will cause a decrease in the viscosity of the polymer while at the same time the formed linear polysiloxane will have terminal silicon-bonded hydroxyl groups.

An alternative method for making the linear organopolysiloxane containing terminal silicon-bonded hydroxyl groups comprises adding water to the high molecular weight polymer described above in such amount that when heated at elevated temperatures, for instance, 150° to 170° C., the viscosity is reduced to the desired level of 50 to 100,000 centipoises. The amount of water used will vary depending upon such factors as the molecular weight of the polymer being treated, the time and temperature at which the mixture of high molecular weight organopolysiloxane and water will be heated, the ultimate viscosity desired, etc.

The amount of water used to reduce the molecular weight can be readily determined. For instance, one can obtain a linear fluid methylpolysiloxane containing terminal silicon-bonded hydroxyl groups and having a viscosity of from 1,000 to 2,000 centipoises at 25° C. by heating a high molecular weight methylpolysiloxane (prepared in accordance with the directions above) of about 2,000,000 centipoise viscosity with only 0.5%, by weight, thereof water for about 2 hours at 150° to 170° C.

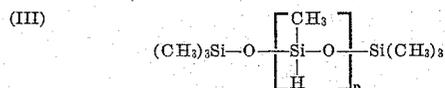
The methyl hydrogen polysiloxane corresponding to the formula



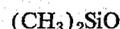
where m and n have the meanings set forth above, may be prepared by any one of several ways. In general, these methyl hydrogen polysiloxanes may be either linear or cyclic polysiloxanes. Thus, these methyl hydrogen

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polysiloxanes, if in linear form, may correspond to the general formula



where p is an integer greater than 1, e.g., 10 to 1,000, or may have intercondensed $CH_3SiO_{3/2}$ units (in very small molar concentrations) intermediate the trimethylsiloxy units, or even intercondensed dimethylsiloxy units having the formula



Generally, when there are dimethylsiloxy units in the methyl hydrogen polysiloxane, the molar concentration of such dimethylsiloxy units should not exceed more than 10 mol percent, and preferably is of the order of from 0 to 5 mol percent of the total number of siloxy units in the linear polysiloxane. Alternatively, the methyl hydrogen polysiloxane may be a cyclic methylpolysiloxane of the formula



where q is a whole number equal to from 3 to 10 or more. More particular directions for preparing the linear methyl hydrogen polysiloxane and the cyclic methyl hydrogen polysiloxane may be found in Wilcock Patent 2,491,843 and in Sauer Patents 2,595,890 and 2,595,891, all of the aforesaid patents being assigned to the same assignee as the present invention.

I have unexpectedly found that contrary to what might be expected, dibutyl tin dilaurate and dibutyl tin diacetate gave minimum migration of the methylpolysiloxane and were able to be used in lower concentrations than when one employed metallic soaps, even tin soaps, such as tin octoate, tin naphthenate, tin oleate, and even such a metallic salt as butyl tin trioctoate, which is closely akin to dibutyl tin dilaurate and dibutyl tin diacetate.

The above essential ingredients used for treating cellulosic materials to render them adhesive in the form of a coating material which is non-migratory as far as the linear methylpolysiloxane containing terminal silicon-bonded hydroxyl groups is concerned, are employed in the form of an aqueous emulsion (with or without solvent contained therein), which can be used as a treating bath for cellulosic materials such as cellulosic sheet material, parchment paper, kraft paper, linen rag paper, rice paper, glassine, cellophane, sulfite cellulose paper, and the like, as well as sheeting or boxing materials, such as paperboard, cardboard, pulpboard, pasteboard.

The aqueous emulsion employed in the practice of the present invention advantageously comprises, by weight, the following:

Polydimethylsiloxane	-----	1 to 35%.
Water	-----	65 to 98%.
Emulsifying agent (e.g., polyvinyl alcohol)	-----	0.1 to 3%.
Methyl hydrogen polysiloxane	-----	0.1 to 5% based on the weight of the polydimethylsiloxane.
Tin (in the form of the dibutyl tin salt)	-----	0.05 to 10% based on the weight of the polydimethylsiloxane.

The amount of the specific dibutyl tin salt employed will depend upon such factors as, for instance, its effect on the stability of the emulsion, the type of polydimethylsiloxane and methyl hydrogen polysiloxane used, the type of paper to which the treating composition will be applied, the solubility of the tin salt, as well as the medium in which the tin salt will be used, the treating conditions including temperature and time of treatment,

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The emulsifying agent used is important if one is to obtain a stable emulsion which, on application to paper, will provide the release required without migration of the polydimethylsiloxane. It has been found unexpectedly that an emulsifying agent which is advantageously employed comprises polyvinyl alcohol, and this emulsifying agent has given satisfactory properties in the treated paper. It has further been found that the usual emulsifying agent, such as Triton X-100 (isooctyl phenyl ether of polyethylene glycol, manufactured and sold by Rohm and Haas Company, Philadelphia, Pa.) and Igepal CO-530 (polyoxyethylated nonyl phenol containing 7 moles ethylene oxide manufactured and sold by Antara Chemicals, Division of General Aniline & Film, New York, N.Y.) are not satisfactory because they undesirably reduce the release characteristics of the treated paper.

The actual amount of emulsifying or dispersing agent employed will depend, for instance, upon the type of ingredients present in the treating composition, the type of emulsifying agent employed, the application intended, etc. Generally, the amount of emulsifying agent satisfactorily employed may range from about 0.1 to 3%, by weight, based on the weight of the entire treating aqueous emulsion. The amount used is not critical and persons skilled in the art will have little difficulty in determining readily the amount which gives optimum results. It is preferably that the emulsifying agent used be one which permits the emulsion to be stable under treating conditions but is readily broken within the interstices of the paper fibers to deposit the organopolysiloxane.

One method for making the emulsion type treating compositions herein described comprises, first, dissolving the emulsifying agent, e.g., polyvinyl alcohol in water, and then adding slowly the polydimethylsiloxane and the methyl hydrogen polysiloxane. This mixture of ingredients is thoroughly homogenized (or colloided) until the polydimethylsiloxane and methyl hydrogen polysiloxane are intimately dispersed throughout the water phase. This material is often referred to as a "master emulsion." An aqueous emulsion using, for example, polyvinyl alcohol as the emulsifying agent, is prepared of the dibutyl tin salt similarly as above except that preferably some solvent, such as xylene, is added to the tin salt prior to its addition to the solution of water and polyvinyl alcohol. This tin salt mixture is also homogenized to form an emulsion and in this form is added to the master emulsion in the preparation of the treating bath. The master silicone emulsion is preferably diluted to use concentrations with an additional amount of water prior to incorporation of the catalyst emulsion.

The procedure described above for preparing water emulsions of the treating compositions herein described may, of course, be varied within wide limits and it is not intended that the description be limiting in any manner. The presence of small amounts of organic solvents is not precluded and under some circumstances may be desirable. If any organic solvent is employed, it is preferable that one employ those which are easily volatilized at the temperature at which treatment of the paper will take place. The emulsion should be kept at a relatively cool temperature, e.g., around room temperature, prior to using in order to maintain its stability.

The final treating mixture can be applied to the paper by any convenient means, for instance, with conventional dip or roller coating equipment, by padding, spraying, knife-coating, etc.; alternatively, the emulsion may be applied by means of a size press employed in combination with a paper machine so that the treatment of the paper is on a continuous basis taking place after the paper is formed on, for instance, a Fourdrinier machine.

Following treatment of the cellulosic material with the emulsion or emulsion-dispersion, the material is advantageously dried by passing the treated paper over

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heated rolls (or "cans") maintained at temperatures of about 90° to 175° C. for from about 10 seconds to 3 minutes or more. The use of circulating hot air at temperatures of from 100° to 160° C. may also be used for times of from 30 seconds to 5 minutes to effect curing of the treated paper. This drying step will bring out the optimum release properties of the paper without further heat treatment. Of equal significance is the fact that these optimum release properties are immediately available without requiring aging or storage of the treated paper. Obviously, the higher the temperature, the shorter the period of exposure of the paper for removing the water and drying the paper.

In order that those skilled in the art may better understand how the present invention may be practiced, the following examples are given by way of illustration and not by way of limitation. All parts and percents are by weight.

The polydimethylsiloxane containing terminal silicon-bonded hydroxyl groups (hereinafter referred to as "polydimethylsiloxane") used in the following examples had a viscosity of about 3,000 centipoises when measured at 25° C. and had a ratio of approximately two methyl groups per silicon atom. This high viscosity composition was obtained by heating octamethylcyclotetrasiloxane with about 0.001%, by weight, thereof of potassium hydroxide for about 2 to 4 hours at about 145° C. until a highly viscous (about 3,000,000 centipoises) benzene-soluble product was obtained having slight flow at room temperature. About 0.5% thereof water was added and the mixture heated for about two hours at 150° to 175° C. until a product having a viscosity of about 3,000 centipoises (when measured at 25° C.) was obtained. This material was a linear fluid polydimethylsiloxane having terminal silicon-bonded hydroxyl groups. A devolatilized polydimethylsiloxane (so designated) was also used wherein all volatiles up to at most 1% were removed by heating the polydimethylsiloxane under vacuum of about 15 mm. at 135° C.

The methyl hydrogen polysiloxane used in the following examples was a linear trimethyl silyl chain-stopped polysiloxane described in Wilcock Patent 2,491,843, and had a viscosity of 100 centipoises when measured at 25° C. This material was obtained by cohydrolyzing 5 parts (CH₃)₃SiCl and 95 parts CH₃SiHCl₂.

In the following tests, the release characteristics of the treated paper (parchment paper was used) were determined by pressing (by hand) a strip of surgical adhesive tape on the surface of the treated paper and lifting the tape from the paper; evaluation of the release was determined by assigning numerical values as follows:

- 0—No lifting of paper whatever
- 1—One edge of paper lifted up to ¼"
- 2—One edge of paper lifted ¼" to 1"
- 3—One edge of paper lifted 1" to 2"
- 4—Paper falls off after being lifted by tape
- 5—Paper shakes off after being lifted by tape
- 6—Paper will not shake off

Migration of the silicone from the treated paper to the surface with which it came in contact was determined by observing the detackification of a surgical adhesive tape (loss of tack of the adhesive) caused by migration of the silicone from the surface of the paper to the adhesive on the tape. This was accomplished by pressing (by hand) a strip of adhesive tape onto the surface of the treated paper five times in five different areas. This technique greatly accelerated determination of migration because the adhesive would be expected to pull off silicone which, if given sufficient time, might migrate of its own accord to the material with which it came in contact. Surgical adhesive tape was used because a major application of release paper is its use as interleaving sheets where the treated paper is in intimate contact with adhesives and

no loss of tack can be tolerated in such an application. A strip of the adhesive tape was then lifted from the paper and folded over so that the adhesive surface (which had been in contact with the release paper) was brought into contact with itself. The pull required to separate the adhesive surface from itself (evaluated subjectively as to poor, fair, fair-good, and good tack) compared with tape which had not been in contact with release paper, was used as a measure of detackification of the tape and thus as a measure of migration of the silicone material. The methylpolysiloxane pickup was within the range from about 0.4% to 2%, by weight, based on the weight of the parchment paper which was treated in every instance in the following examples.

EXAMPLE 1

This example illustrates the preparation of treating baths in the form of emulsions employing a high viscosity polyvinyl alcohol manufactured and sold by E. I. du Pont de Nemours Co., Wilmington, Delaware, under the name Elvanol 50-42, and made by partially hydrolyzing polyvinyl acetate (86-89% hydrolyzed). A master emulsion was prepared by mixing together on a weight basis, based on the total weight of the emulsion, amounts of the devolatilized hydroxy chain-stopped polydimethylsiloxane ranging from 28.5 to 30%, from 0.3 to 1.5% of the methyl hydrogen polysiloxane, and from 0.63 to 1.26% polyvinyl alcohol (as the emulsifying agent). In some instances, xylene was added to the mixture of ingredients. This mixture was then diluted further with water to make the total percent weight equal to 100%, and passed through a homogenizer to obtain a homogeneous creamy emulsion. Each emulsion was thereafter mixed with an aqueous emulsion of the organometallic salt employed in each instance, and this mixture was further diluted with water and intimately mixed to give a homogeneous emulsion treating bath in which the total weight of the polydimethylsiloxane and the methyl hydrogen polysiloxane comprised about 10%, by weight, of the total emulsion treating bath. The particular dibutyl tin salt used was employed in such amount that there was present in the treating bath composition from 0.2 to 0.4% tin, based on the total weight of the polydimethylsiloxane and methyl hydrogen polysiloxane. Tables IA and IB below show the effects on treated parchment paper which was immersed in the emulsion bath, the treated paper removed and passed between squeeze rolls to remove excess treating composition, and thereafter the paper was dried by passing it over a heated cylindrical roll maintained at a temperature of from 110°-113° C. for about 3 minutes. This method for treatment of parchment paper was followed in all the following examples as well:

Table IA

MASTER SILICONE EMULSION

Test No.	Weight Percent Polydimethylsiloxane	Weight Percent Methyl Hydrogen Polysiloxane	Weight Percent Xylene	Weight Percent Polyvinyl Alcohol
1	30			0.63
2	28.5	1.5		0.63
3	30			1.26
4	29.7	0.3		1.26
5	28.5	1.5		1.26
6	30		7.5	1.26
7	28.5	1.5	7.5	1.26
8	30		7.5	1.26
9	28.5	1.5	7.5	1.26
10	^a 30		7.5	1.26
11	^a 28.5	1.5	7.5	1.26
12	^a 30		7.5	1.26
13	^a 28.5	1.5	7.5	1.26

^a This was the non-devolatilized hydroxy chain-stopped polydimethylsiloxane.

Table IB

TREATING BATH COMPOSITION^b

Test No.	Catalyst	Catalyst Concentration	Performance on Paper	
			Release	Tack
1	Dibutyl tin dilaurate	0.4	0	Poor.
2	do	0.4	0	Good.
3	do	0.4	0	Poor.
4	do	0.4	0	Good.
5	do	0.4	0	Do.
6	do	0.2	1-2	Poor.
7	do	0.2	0	Good.
8	Dibutyl tin diacetate	0.2	0-1	Poor.
9	do	0.2	0	Good.
10	Dibutyl tin dilaurate	0.2	0	Poor.
11	do	0.2	0	Good.
12	Dibutyl tin diacetate	0.2	1	Poor.
13	do	0.2	0	Good.

^b All treating baths contained 10%, by weight, methylpolysiloxane of the combined devolatilized polydimethylsiloxane and the methyl hydrogen polysiloxane.

EXAMPLE 2

In this example, a master emulsion was prepared similarly as in Example 1, employing on a weight basis 28.5% of the devolatilized hydroxy chain-stopped polydimethylsiloxane, 1.5% of the trimethylsilyl chain-stopped methyl hydrogen polysiloxane, 7.5% xylene, 1.26% polyvinyl alcohol, and the balance (up to 100%) water. The treating bath composition (made by diluting the master emulsion) used to treat the parchment paper again comprised, as in Example 1, 10 weight percent of the mixture of the hydroxy chain-stopped methylpolysiloxane and the methyl hydrogen polysiloxane, and dibutyl tin dilaurate as a catalyst. Three treating bath compositions were prepared, of which the emulsions used for treating purposes contained varying amounts of catalyst concentration of dibutyl tin dilaurate, which was added in the form of an emulsion similarly as in Example 1. The amounts of catalyst used were 0.2% tin, 0.4% tin, and 4.0% tin, each in the form of dibutyl tin dilaurate. The treated paper was treated and dried similarly as was done in Example 1, and its performance as to release and tack were determined. It was found that regardless of the catalyst concentration, the release in each of the three instances was 0, and the tack was "Good." This example illustrates the wide range of catalyst concentration which can be employed in the practice of the present invention.

The following example illustrates that the incorporation of a solvent such as xylene (benzene, toluene, etc., can also be used) in the treating emulsion improves the stability of the emulsion, and thus allows the treating bath to remain effective over a longer period of time with retention of optimum properties in the treated paper.

EXAMPLE 3

In this example, master silicone emulsions were prepared similarly as in Example 1, and each of these master silicone emulsions was mixed with a catalyst emulsion in which the catalyst was dibutyl tin dilaurate; this emulsion mixture was diluted with water to give a treating bath emulsion composition which was used to treat parchment paper similarly as was done in Example 1. In all the master emulsions, 1.26% polyvinyl alcohol was used as the emulsifying agent, based on the weight of the emulsion. The concentration of the tin catalyst, 0.2% tin in the form of dibutyl tin dilaurate, was based on the total weight of the two polysiloxanes in the emulsion. The following Table IIA shows the composition of the master silicone emulsion, the balance of the emulsion being water. Table IIB shows the performance data on paper treated with the emulsions after the emulsion baths had been allowed to remain at room temperature for various lengths of time; also Table IIB shows the condition of the baths, i.e., their stability, after they were

pumped through pumping equipment as might be encountered in plant usage where the emulsion may be prepared in one part of the plant and then pumped to another part of the plant where it is to be used.

Table IIA
MASTER SILICONE EMULSION

Test No.	Weight Percent Devolatilized Polydimethylsiloxane	Weight Percent Methyl Hydrogen Polysiloxane	Weight Percent Xylene
14	28.5	1.5	
15	28.5	1.5	
16	28.5	1.5	
17	28.5	1.5	
18	28.5	1.5	7.5
19	28.5	1.5	7.5
20	28.5	1.5	7.5
21	28.5	1.5	7.5
22	28.5	1.5	06.0
23	28.5	1.5	06.0
24	28.5	1.5	06.0
25	28.5	1.5	06.0
26	28.5	1.5	07.5
27	28.5	1.5	07.5
28	28.5	1.5	07.5
29	28.5	1.5	07.5

* The solvent used in these instances was mineral spirits.

Table IIB
TREATING BATH COMPOSITION

Test No.	Age of Treating Bath (Hours)	Performance on Paper		Bath Stability to Pumping
		Release	Tack	
14	0	0	Good	Gummed up in 2 hours.
15	1	0	do.	
16	2	0	do.	
17	2 1/4	1	do.	
18	0	0	do.	Very slight gum formation.
19	1	0	do.	
20	2	0	do.	
21	4	0	do.	
22	0	0	do.	Good—no gum.
23	1	0	do.	
24	2	0	do.	
25	4	0	do.	
26	0	0	do.	
27	1	0	do.	
28	2	0	do.	
29	4	0	do.	

This example illustrates the importance of choosing the proper emulsifying agent. As pointed out above, polyvinyl alcohol is admirably suited for the purpose. However, it should be noted from the following example that all non-ionic emulsifiers, of which polyvinyl alcohol is an example, are not satisfactory.

EXAMPLE 4

In this example, master silicone emulsions were prepared similarly as was done in Example 1 and the other examples, employing on a weight basis 28.5% of the devolatilized hydroxy chain-stopped polydimethylsiloxane, 1.5% of the trimethylsiloxy chain-stopped methyl hydrogen polysiloxane, and 7.5% xylene, the balance being water with the exception of the emulsifying agent which was used in small, stipulated amounts. Various emulsifying agents were employed to make the master silicone emulsion. The following Table III shows the particular emulsifier used, the concentration of the emulsifier in the master silicone emulsion, as well as the performance data of the particular treating baths, depending upon the specific emulsifying agent employed. In making the treating bath emulsion compositions (pursuant to the procedure in Example 1), the diluted master silicone emulsions contained 10%, by weight, of the mixture of the devolatilized polydimethylsiloxane and the methyl hydrogen polysiloxane, together with 0.2%, by weight, based on the weight of the mixture of the methylpolysiloxanes of tin, in the form of dibutyl tin dilaurate.

Table III

Test No.	Emulsifier	Weight Percent Emulsifier	Performance on Paper	
			Release	Tack
5				
30	Polyvinyl alcohol (non-ionic).	0.68	0	Good.
31	do.	1.26	0	Do.
32	do.	2.52	0	Do.
10				
33	Mixture of polyoxyethylated nonyl phenols (non-ionic).	1.0	4	Do.
34	Fatty alcohol amine sulfate (anionic).	1.0	0	Do.
35	do.	2.0	0	Do.
36	Sulfonated methyl oleate (anionic).	1.0	1-3	Fair.
15				
37	Alkyl quaternary ammonium chloride (cationic).	1.0	4	Good.
38	Dialkyl quaternary ammonium chloride (cationic).	1.0	1	Do.

EXAMPLE 5

This example illustrates the versatility of using various concentrations of the mixture of the hydroxy chain-stopped methylpolysiloxane and the methyl hydrogen polysiloxane in a treating bath composition. More particularly, a master silicone emulsion was prepared similarly as was done in Example 1, by mixing together 28.5% of the devolatilized hydroxy chain-stopped methylpolysiloxane, 1.5% of the methyl hydrogen polysiloxane, 7.5% xylene, 1.26% polyvinyl alcohol, and the balance (up to 100%) water. This master silicone emulsion was then diluted further with water in such quantities that the mixture of the two polysiloxanes in the master silicone emulsion ranged from about 6 to 30%, by weight, of the total weight of the treating emulsion, employing in each instance 0.2%, by weight, tin based on the weight of the two polysiloxanes, in the form of dibutyl tin dilaurate. Parchment paper was treated similarly as was done in Example 1 and the performance of the treated paper was determined as evidenced by its release and tack. The following Table IV shows the concentration of the mixture of polysiloxanes in the treating bath composition as well as the release and tack of the treated paper.

Table IV

Test No.	Weight Percent Polysiloxanes in Treating Bath Emulsion	Release	Tack
45			
39	6	1	Good.
40	10	0	Do.
41	15	0	Do.
42	30	0	Do.

The following example illustrates that good release with no silicone migration is obtained over a wide range of viscosity of the hydroxy chain-stopped polydimethylsiloxane polymers. The range of viscosity evaluated, 600 centipoises to 94,500 centipoises, measured at about 25° C., is not intended to exclude lower and higher viscosities.

EXAMPLE 6

In this example, various master silicone emulsions were prepared from the devolatilized hydroxy chain-stopped methyl polysiloxanes employing in each instance on a weight basis 28.5% of the hydroxy chain-stopped methylpolysiloxane, 1.5% of the methyl hydrogen polysiloxane, 7.5% xylene, and 1.26% polyvinyl alcohol as the emulsifying agent, the balance being water. In making the master silicone emulsions, various viscosities of the hydroxy chain-stopped methylpolysiloxanes were employed. Each master silicone emulsion was thereafter diluted further with water to obtain a treating bath composition, of which 10%, by weight, comprised the mixture of the devolatilized polydimethylsiloxane and the methyl hydrogen polysiloxane; to this was added about 0.2%, by weight, tin based on the combined weight of

the mixture of the polydimethylsiloxane and methyl hydrogen polysiloxane, in the form of dibutyl tin dilaurate. The following Table V shows the viscosities of the various hydroxy chain-stopped polydimethylsiloxanes, as well as the results of release and tack tests carried out on paper treated with the various treating emulsions pursuant to the method described in Example 1.

Table V

Test No.	Viscosity, Centipoises	Release	Tack
43	600	0	Good.
44	3,700	0	Do.
45	27,500	0	Do.
46	94,500	0	Do.
47	14,000	0	Do.

¹ This polydimethylsiloxane was not devolatilized.

Although the preceding examples have given formulations which can advantageously be used in the practice of the present invention, the following general formulations may also be helpful in determining the relationship of the master emulsion system, the catalyst emulsion, and the actual treating emulsion. Thus, the master emulsion may generally comprise the following ingredients, by weight:

- 28.50 parts of the hydroxy chain-stopped polydimethylsiloxane (whether devolatilized or non-devolatilized)
- 1.50 parts of the trimethylsiloxy chain-stopped methyl hydrogen polysiloxane (or cyclic methyl hydrogen polysiloxane)
- 1.26 parts polyvinyl alcohol (or varied as the case may be)
- 7.50 parts xylene or mineral spirits (or varied as the case may be)
- 61.24 parts water
- 100.00 parts total

The tin salt emulsion may comprise the following ingredients, by weight:

- 70.0 parts of the tin salt, for instance, dibutyl tin dilaurate (18% tin)
- 30.0 parts xylene
- 2.1 parts polyvinyl alcohol
- 107.9 parts water
- 210.0 parts total

The treating bath emulsion in general used to treat the parchment paper may comprise the following:

- 33.30 parts of the master silicone emulsion
- 0.33 parts of the catalyst emulsion
- 66.37 parts water
- 100.00 parts total

It will be apparent that the above relationship of ingredients in the master emulsion, the catalyst emulsion, and the treating bath emulsion may be varied pursuant to the modifications and variations defined in the preceding examples.

It will, of course, be apparent to those skilled in the art that in addition to the hydroxy chain-stopped methyl polysiloxane of the viscosities recited in the foregoing examples, other linear hydroxy chain-stopped polydimethylsiloxanes (both devolatilized and non-devolatilized) containing terminal silicon-bonded hydroxyl groups of other viscosities within the range of 50 to 2,000,000 centipoises, when measured at 25° C., can be employed without departing from the scope of the invention. The concentration of the hydroxy chain-stopped polydimethylsiloxane, the methyl hydrogen polysiloxane, the type of methyl hydrogen polysiloxane employed, as well as the concentration of the catalyst, emulsifying agent, etc., may vary within the ranges previously recited within the

scope of the present invention. The concentration of the dibutyl tin dilaurate or dibutyl tin diacetate (or mixtures of such tin salts) also may be varied within wide limits depending on the factors recited previously.

The amount of organopolysiloxane which is picked up by the cellulosic paper material as a result of the treatment with the emulsion of the organopolysiloxanes depends upon such factors as the absorbcency of the cellulosic material, the method of application, the concentration of organopolysiloxanes in the emulsion, etc. Generally, the amount of organopolysiloxane pickup ranges from about 0.1 to about 5%, or more, based on the dry weight of the cellulosic material, the preferred pickup being within the range of about 0.4 to 2% organopolysiloxane. Obviously, larger amounts or organopolysiloxane pickup may be employed, but generally this is not necessary and usually serves merely to increase the cost of the treatment.

Advantages of using the compositions herein described for the above specified purposes are manifold. Of particular importance is the fact that when the above combination of ingredients is applied to paper, in addition to imparting adhesive characteristics thereto, the organopolysiloxane (that is, the polydimethylsiloxane and the methyl hydrogen polysiloxane) content in the paper is substantially non-migratory and will not affect or be transferred to the surfaces of compositions from which the adhesive paper must be readily separated. Moreover, the adhesive characteristics of the treated paper are substantially the same even after the paper is stored for long periods of time; in contrast to this, paper treated with prior organopolysiloxane compositions used to render the paper adhesive have suffered severe losses in their adhesive properties after storage for any length of time, for instance, even after only 6 months.

Of equal significance is the fact that paper treated in accordance with my process can be employed at once for its anti-release purposes with realization of essentially optimum properties. Heretofore, organopolysiloxanes previously available on the market for the same purpose required aging, that is, storing of the treated paper for times as long as six weeks, in order to bring out the optimum release characteristics of the treated paper. Of considerable importance is the fact that even at high temperatures, the release characteristics are maintained at optimum levels and elevated temperatures do not destroy the release film.

The compositions for treating cellulosic materials herein described are readily amenable to a single-step procedure and are easily regulated and controlled for adjustable organopolysiloxane pickup by minor variations in formulations. Standard paper making or paper converting equipment is readily employed in connection with the treating operations and no precautions need be taken for any toxic materials which may be contained in the treating emulsions.

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 containers fashioned from the treated paper or paperboard, and after cooling it will be found that solidified asphalt or polymer is readily and cleanly separated from container walls.

My invention permits paper treated in accordance with my process to be substituted for various materials which have heretofore been used in contact with adhesive surfaces of electrician's pressure sensitive tape, adhesive tapes used for surgical purposes, and regenerated cellulose tapes carrying a permanent adhesive upon one surface. Vulcanized or unvulcanized sheets of rubber can be prevented from adhering to each other despite the fact that these sheets of rubber are 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 prebaked goods, such

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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 I claim as new and desire to secure by Letters Patent of the United States is:

1. The method for rendering cellulosic fibrous sheet material non-adherent to surfaces which normally adhere thereto, which process comprises treating the cellulosic fibrous sheet material with an aqueous emulsion treating bath containing, by weight, the following sole active ingredients:

- (a) from 1 to 35% of a linear polydimethylsiloxane containing terminal silicon-bonded hydroxy groups,
- (b) from 65 to 98% water,
- (c) from 0.1 to 5% of a methyl hydrogen polysiloxane, based on the weight of (a),
- (d) from 0.05 to 10% tin in the form of a metallic salt selected from the class consisting of dibutyl tin dilaurate and dibutyl tin diacetate, based on the weight of (a),
- (e) from 0 to 10% of an organic solvent, and
- (f) from 0.1 to 3% of polyvinyl alcohol as an emulsifying agent, and thereafter drying the treated material.

2. The method for rendering cellulosic fibrous sheet material non-adherent to surfaces which normally adhere thereto, which process comprises treating cellulosic fibrous sheet material with an aqueous emulsion treating bath containing, by weight, the following sole active ingredients:

- (a) from 1 to 35% of a linear polydimethylsiloxane containing terminal silicon-bonded hydroxy groups,
- (b) from 65 to 98% water,
- (c) from 0.1 to 5% of a linear methyl hydrogen polysiloxane, based on the weight of (a),

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- (d) from 0.05 to 10% tin as dibutyl tin dilaurate, based on the weight of (a),
- (e) from 0 to 10% of an organic solvent, and
- (f) from 0.1 to 3% of polyvinyl alcohol as an emulsifying agent, and thereafter drying the treated material.

3. The method for rendering cellulosic fibrous sheet material non-adherent to surfaces which normally adhere thereto, which process comprises treating the cellulosic fibrous sheet material with an aqueous emulsion treating bath containing, by weight, the following sole active ingredients:

- (a) from 1 to 35% of a linear polydimethylsiloxane containing terminal silicon-bonded hydroxy groups,
- (b) from 65 to 98% water,
- (c) from 0.1 to 5% of a linear methyl hydrogen polysiloxane, based on the weight of (a),
- (d) from 0.05 to 10% tin as dibutyl tin diacetate, based on the weight of (a),
- (e) from 0 to 10% of an organic solvent, and
- (f) from 0.1 to 3% of polyvinyl alcohol as an emulsifying agent, and thereafter drying the treated material.

4. Cellulosic material treated in accordance with the method described in claim 2.

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