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RENDERING CELLULOSIC MATERIAL NON-ADHERENT TO ADHESIVES

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The present invention relates to methods of rendering cellulosic fibrous sheet material non-adherent to various organic solids. It is particularly concerned with methods of rendering paper or paperboard non-adherent to normally adherent material such as asphalt, rubber, and high molecular weight organic polymers.

Cellulosic materials impermeable to asphalt have heretofore been prepared by depositing a double coating upon the cellulosic material. The first coating was of clay; the second, of methylcellulose and starch. A method such as this, however, is expensive and changes the physical nature of the material to which it is applied.

It is an object of the present invention to provide an improved method for rendering cellulosic fibrous sheet material non-adherent toward materials which normally adhere thereto. Further objects are to provide non-adherent cellulosic sheet material of improved water-repellency and grease-proof characteristics.

It is known that a methylhydrogenpolysiloxane fluid may be cured on a surface to render that surface water-repellent.

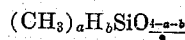
It has now been found that the cured methylhydrogenpolysiloxane also renders a surface highly non-adherent toward materials which normally adhere thereto, and that this property can be enhanced by incorporating a water soluble cellulose ether into the polysiloxane prior to curing. When the cellulose ether is present, a given degree of non-adherency can be attained with only a fraction of the amount of siloxane which would otherwise be needed. Hence, incorporation of the cellulose ether into the polysiloxane results in a process which is much more economical and more practical on a commercial scale.

In accordance with a preferred form of this invention, a cellulosic sheet material is wetted with an aqueous emulsion of a methylhydrogenpolysiloxane fluid in an aqueous solution of a water-soluble cellulose ether, and the material dried. The material becomes water-repellent, greaseproof, and extremely non-adherent toward normally adhesive materials. These desirable properties are imparted to the cellulosic sheet material without any apparent change in texture or color, and without altering such physical properties as tensile strength, tear resistance, or moisture vapor transmission.

The cellulosic materials of concern herein include all types of papers, such as kraft paper, linen rag paper, rice paper, sulfite cellulose paper and the like; and sheeting or boxing materials such as paperboard, cardboard, pulpboard, and pasteboard.

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The methylhydrogenpolysiloxane fluids employed in the process of this invention are fluids of the empirical formula



in which a has a value of from 1.0 to 1.5, b has a value of from 0.75 to 1.25, and the sum of a and b has a value of from 2.0 to 2.25 inclusive. They may contain traces of hydroxy radicals due to incomplete condensation, and can be either cyclic or linear polymers. At least 50 per cent of the siloxane units present in the polymer are of the formula CH_3HSiO . The linear polymers may be end-blocked with units such as trimethylsiloxy or dimethylhydrogensiloxy units. Such fluids are well known to the art.

Any of the water soluble cellulose ethers may be used in the process of this invention. Methylcellulose, hydroxyethylcellulose, and the sodium salt of carboxymethylcellulose (the glycolic acid ether of cellulose) are preferred. Ethylcellulose may also be used when it is water soluble, i. e. when it has a degree of substitution (average number of ethyl groups per anhydro-glucose unit) of from 0.8 to 1.3. When methylcellulose is used, a viscosity grade of from 15 cps. (centipoises) to 4,000 cps. is preferable. This indication of viscosity grade is the viscosity of a 2 per cent aqueous solution at 20° C.

A preferred mode of operation in the process of this invention is to prepare a stock of an aqueous emulsion of the methylhydrogenpolysiloxane fluid. This stock emulsion is then diluted with the aqueous solution of the cellulose ether as needed. The final mixture preferably contains from 0.1 to 20 per cent by weight of the polysiloxane, and from 0.1 to 10 per cent by weight of the cellulose ether. Dilution of the polysiloxane emulsion with the cellulose ether solution requires no special equipment since the two are readily compatible. If desired, rather than diluting the methylhydrogenpolysiloxane stock emulsion with the cellulose ether solution, the working emulsion may be prepared directly by emulsifying the methylhydrogenpolysiloxane fluid in the cellulose ether solution.

In preparing an aqueous emulsion of the methylhydrogenpolysiloxane fluid, it is preferable to use a colloid mill or other very high speed mixer. Any conventional emulsifying agent may be used with satisfactory results. For improved water repellency in the treated product, however, it is preferred to employ quaternary ammonium salts or the higher aliphatic alcohol sul-

phates. The amount of the emulsifying agent used in the emulsion will, of course, depend upon the particular agent used. When a higher aliphatic alcohol sulphate is used, it is preferred to employ about 10 per cent by weight based on the amount of methylhydrogenpolysiloxane fluid present. When this emulsion is to be used primarily as a stock emulsion, to be diluted with the solution of cellulose ether prior to its actual use, any convenient ratio of methylhydrogenpolysiloxane to water may be used. For ease of preparation and convenience in storing, a concentration of about 50 per cent polysiloxane is preferable. The methylhydrogenpolysiloxane emulsions tend to liberate hydrogen upon standing. It is accordingly desirable to add an organic acid such as acetic acid to the emulsion in order to inhibit such evolution of silane hydrogen.

Catalysts may be incorporated into the emulsion to speed up the curing rate of the methylhydrogenpolysiloxane fluid. A wide choice of such catalysts is available, since any metal salt of a carboxylic acid is applicable. The lead, iron, and zinc salts of carboxylic acids are preferred, particularly the acetates, hexoates, octoates, oleates, stearates, naphthenates, laurates, and resinates. The copper, aluminum, magnesium, cadmium, cobalt, nickel and sodium salts are also effective. Catalysts such as sodium bicarbonate and sodium aluminate may also be used. The catalyst is preferably employed in such an amount that there is from 0.5 to 4.0 per cent by weight of the metal constituent present, based on the weight of the siloxane. The catalyst should be added just prior to the application of the emulsion.

The final emulsion mixture can be applied to the material to be treated by any convenient method. When applied to paper, the conventional dip or roller coating equipment may be used, or the emulsion may be applied on a size press connected with the paper machine.

The amount of siloxane polymer which is picked up by the material to be treated depends upon the absorbency of the material, the application method, and the concentration of siloxane in the emulsion. The pickup desirable for optimum non-adherency and water-repellency properties will vary with the type of cellulosic material being treated. Ordinarily, the preferred pickup of siloxane is from 0.25 to 4.0 per cent, based on the dry weight of the cellulosic material, and the preferred pickup of cellulose ether is from 0.1 to 3.0 per cent. Of course a greater pickup may be used, but it is not ordinarily necessary and would only increase the expense of the product.

Following the wetting of the cellulosic material, it is dried. This drying step also results in the release of hydrogen from the methylhydrogenpolysiloxane fluid and its attendant cure. This drying or curing can be accomplished at room temperature, but in order to speed up the process and to develop maximum non-adherency immediately, it is preferable to apply heat. In general, a temperature of from 40° to 200° C. is preferred, with longer times of exposure being used at the lower temperatures. A period of from 20 to 180 seconds at 150° C. has been found adequate to completely dry and cure the wetter material when a catalyst is present.

Cellulosic materials treated as described above have a wide range of utility. For instance, asphalt or high molecular weight organic polymers

such as polyisobutylene may be poured hot into containers fashioned from the treated paper or paperboard. After cooling, the solidified asphalt or polymer is easily and cleanly separated from the container walls.

Paper treated in accordance with this invention may be used in contact with the 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. Various types of fabrics, such as Holland cloth and open weave heavily starched fabrics, have heretofore been used for this purpose. This invention allows treated paper to be substituted for the indicated fabrics at a very considerable saving in cost.

A still further aspect of the present invention involves the use of paper treated as described to prevent sheets of either vulcanized or unvulcanized rubber from adhering together. Thus, rubber compounded in the customary fashion in a rubber mill is sheeted out and stored as sheets. These sheets are sticky and cohere, forming a solid mass. When a sheet of paper treated as described is placed between the sheets of rubber, each sheet may be removed separately and individually without difficulty from sticking. In connection with vulcanized rubber, vulcanized sheet rubber could advantageously be cut by stacking sheets of rubber and die-cutting through all the sheets at once, except that this would result in the various sheets sticking together. By interposing treated paper, this sticking is prevented. Many similar interleaving uses such as this are practical with paper treated in accordance with this invention.

Paper treated in accordance with this invention is also useful in lining boxes of partially pre-baked goods such as buns, rolls, and the like. Thus, the partially baked goods may be finished off in the original container and when baking is completed, good release is obtained from the liner.

The process of this invention may also be applied to textile fabrics to develop non-adherent properties thereon.

The following examples describe specific embodiments of the invention, but are not to be construed as limiting the scope thereof. All parts given are by weight.

For use in these examples, a master batch of the methylhydrogenpolysiloxane emulsion was made as follows.

A mixture of 1,000 parts of $\text{CH}_3\text{HSiCl}_2$ and 51.5 parts of $(\text{CH}_3)_2\text{SiCl}$ was added to 750 parts of benzene. This mixture was then cooled to 20° C. To this mixture 675 parts of isopropyl alcohol were added over a period of 10 minutes, and then 783 parts of water were added over a period of one hour. An additional 750 parts of benzene were then added to the reaction mixture. The product was washed six times with water and strip distilled at 3 mm. pressure to 115° C. to remove the benzene and the lower boiling products. There were obtained 500 parts of a trimethylsiloxane end-blocked methylhydrogenpolysiloxane. The 500 parts of methylhydrogenpolysiloxane fluid were slowly added, with extremely rapid agitation, to a solution of 50 parts of a higher aliphatic alcohol sulphate ("Dupanol G") in 150 parts of water. The resulting emulsion was diluted with 300 parts of water, to give a 50 per cent concentration of the polysiloxane. About 3 parts of glacial acetic acid were then added, to reduce the pH of the emulsion to about

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6. This emulsion is designated hereafter as emulsion A.

A master batch of zinc 2-ethyl hexoate catalyst emulsion was prepared as follows. Fifty parts of an 8 per cent solution (based on zinc metal) of zinc 2-ethyl hexoate in naptha were added with extremely rapid agitation to a solution of 5 parts of "Dupanol G" in 15 parts of water. The resulting emulsion was diluted with 30 parts of water, giving an emulsion which contained 4 per cent by weight of zinc metal. This emulsion is designated hereafter as emulsion B.

Example 1

A 1.5 per cent aqueous solution of a 4,000 cps. grade of methylcellulose was prepared. 185 grams of this solution were added to a mixture of 12 grams of emulsion A and 3 grams of emulsion B, giving an emulsion which contained 3 per cent by weight of the siloxane and 1.4 per cent of the methylcellulose. A sheet of 0.023" kraft paperboard was dipped in this emulsion and passed between squeeze rolls to remove the excess. The gain in weight represented 0.33 per cent pickup of siloxane. The board was dried for one minute at 150° C. When molten asphalt at 350° F. was poured into a container fashioned from this treated board and allowed to cool, excellent release was obtained with no adhesion of cellulose fibers to the asphalt.

For purposes of comparison, three grams of the zinc catalyst emulsion B and 185 grams of water were added to 12 grams of the 50 per cent methylhydrogensiloxane emulsion A, giving an emulsion which contained 3 per cent by weight of the siloxane. A sheet of 0.023" kraft paperboard, weighing 7.35 grams, was dipped in this emulsion and passed between squeeze rolls to remove the excess. After squeezing, the weight was found to be 10.78 grams, representing a 1.4 per cent pickup of the siloxane. The board was then dried for one minute at 150° C. Asphalt at 350° F. was poured into a container fashioned from this treated board. Upon cooling, the asphalt adhered to the board in many areas. When release was forced, the surfaces of the solidified asphalt which had been in contact with the container were contaminated with cellulose fibers.

Example 2

A mixture was made of 40 grams emulsion A, 10 grams emulsion B, 67 grams of the 1.5 per cent aqueous solution of 4,000 cps. grade methylcellulose, and 83 grams of water. The resulting emulsion contained 10 per cent by weight of the siloxane and 0.5 per cent of the methylcellulose. A 7.39 gram sample of the 0.023" kraft paperboard was dipped in this emulsion and then squeezed, giving a weight of 8.56 grams. This represents 1.6 per cent pickup of the siloxane. The board was cured for one minute at 150° C., and excellent release from asphalt was obtained.

Example 3

A 6 per cent solution of a 50 cps. grade methylcellulose was prepared. 75 grams of this solution were added to a mixture of 20 grams emulsion A and 5 grams emulsion B. The resulting emulsion contained 10 per cent by weight of the siloxane and 4.5 per cent of the methyl cellulose. After dipping and squeezing, an 8.13 gram sample of the .023" kraft paperboard weighed 9.51 grams, representing a 1.7 per cent pickup of the siloxane. Molten asphalt was poured into a container fashioned from this treated board

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and allowed to cool. Excellent release of the asphalt from the board was obtained.

Example 4

A 4 per cent solution of 50 cps. grade methylcellulose was prepared. 75 grams of this solution were added to 16 grams of emulsion A, 4 grams of emulsion B, and 5 grams of water. The resulting emulsion contained 8 per cent of the siloxane and 3 per cent of the methylcellulose. A 7.59 gram sample of the .023" kraft paperboard, after dipping in this emulsion and squeezing, weighed 8.82 grams, representing 1.3 per cent pickup of the siloxane. After curing the board one minute at 150° C., excellent release from asphalt was obtained.

Example 5

A 7 per cent aqueous solution of 15 cps. grade methylcellulose was prepared. 75 grams of this solution were added to 20 grams of emulsion A and 5 grams of emulsion B. This gave an emulsion containing 10 per cent of the siloxane and 5.3 per cent of the methyl cellulose. When an 8.4 gram sample of the kraft paperboard was dipped in this emulsion and squeezed, a weight of 9.97 grams was obtained, indicating a 1.9 per cent pickup of the siloxane. The board was then cured for two minutes at 150° C. Good release from asphalt was obtained.

Example 6

A 1.5 per cent aqueous solution of 4,000 cps. grade methylcellulose was prepared. 95 grams of this aqueous solution were added to a mixture of 4 grams of emulsion A and 1 gram of emulsion B. The resulting emulsion contained 2 per cent of the siloxane and 1.4 per cent of the methylcellulose. A 2.71 gram sample of kraft paper was dipped in this emulsion and squeezed to remove the excess. The wet weight of the paper was 7.04 grams, indicating a 3.2 per cent pickup of the siloxane and 2.2 per cent pickup of the methylcellulose. The paper was cured for one minute at 150° C. This paper was contacted with a sheet of low tensile crude rubber for a period of 5 days at room temperature under a pressure of 5 lbs. per square inch. No adhesion was obtained between the paper and the rubber.

Example 7

To a mixture of 1.8 grams of emulsion A and 0.5 grams of emulsion B was added 97.7 grams of the 1.5 per cent methylcellulose solution from Example 6. A 2.49 gram sample of kraft paper was dipped in this solution and squeezed, giving a weight of 6.05 grams. This indicated a 1.3 per cent pickup of the siloxane and a 2.1 per cent pickup of the methylcellulose. The paper was cured for one minute at 150° C. and contacted with the crude rubber as in Example 6. Excellent release between the paper and the rubber was obtained.

Example 8

A one per cent aqueous solution of carboxymethylcellulose (sodium salt) was prepared. 97.5 grams of this solution were added to a mixture of 2 grams of emulsion A and 0.5 gram of emulsion B. A sheet of kraft paper was dipped in this emulsion and squeezed. A 1.2 per cent pickup of the siloxane and a 1.10 per cent pickup of the carboxymethylcellulose were obtained. A portion of the treated paper was air-dried for one hour. Another portion was cured for one minute at 150° C. "Scotch Tape" would not adhere to either portion.

Example 9

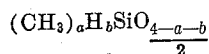
Samples of kraft paper and parchment paper were treated with the emulsion prepared in Example 8. A 1.7 per cent pickup of siloxane was obtained on the kraft paper, and a 1.07 per cent pickup was obtained on the parchment paper. Both papers were cured for one minute at 150° C., placed in contact with sheets of uncured butyl rubber, and subjected to a pressure of 1.3 lbs. per square inch for a period of 48 hours at a temperature of from 110° to 120° F. Both papers showed good release from the rubber.

Example 10

Emulsions of iron octoate and lead naphthenate were prepared, using the procedure employed for the preparation of emulsion B. Each emulsion was adjusted to a 4 per cent by weight content of metal. When Example 6 was repeated, replacing the zinc catalyst with either the iron or lead salts from above, the results comparable with those obtained in Example 6.

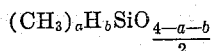
That which is claimed is:

1. The method of rendering cellulosic fibrous sheet material non-adherent toward materials which normally adhere thereto which comprises wetting the material with an aqueous emulsion of a methylhydrogenpolysiloxane fluid of the empirical formula



in which a has a value of from 1 to 1.5, b has a value of from 0.75 to 1.25, and the sum of a and b has a value of from 2.0 to 2.25 inclusive, in an aqueous solution of a water soluble cellulose ether; said emulsion containing from 0.1 to 20 per cent by weight of the methylhydrogenpolysiloxane fluid and from 0.1 to 10 per cent by weight of the cellulose ether; and drying the wetted material.

2. The method of rendering cellulosic fibrous sheet material non-adherent toward materials which normally adhere thereto which comprises wetting the material with an aqueous emulsion of a methylhydrogenpolysiloxane fluid of the empirical formula

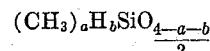


in which a has a value of from 1 to 1.5, b has a value of from 0.75 to 1.25, and the sum of a and b has a value of from 2.0 to 2.25 inclusive, in an

aqueous solution of a water soluble cellulose ether; said emulsion containing from 0.1 to 20 per cent by weight of the methylhydrogenpolysiloxane fluid, from 0.1 to 10 per cent by weight of the cellulose ether, and a metallic salt of a carboxylic acid; and drying the wetted material.

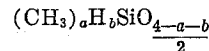
3. The method of claim 2 wherein the cellulose ether is selected from the group consisting of methylcellulose and the sodium salt of carboxymethylcellulose, and the metallic salt is selected from the group consisting of the carboxylates of lead, zinc, and iron.

4. A composition for rendering cellulosic fibrous sheet material non-adherent toward materials which normally adhere thereto, comprised of an aqueous emulsion of a methylhydrogenpolysiloxane fluid of the empirical formula



in which a has a value of from 1 to 1.5, b has a value of from 0.75 to 1.25, and the sum of a and b has a value of from 2.0 to 2.25 inclusive, in an aqueous solution of a water soluble cellulose ether; said emulsion containing from 0.1 to 20 per cent by weight of the methylhydrogenpolysiloxane fluid and from 0.1 to 10 per cent by weight of the cellulose ether.

5. A composition for rendering cellulosic fibrous sheet material non-adherent toward materials which normally adhere thereto, comprised of an aqueous emulsion of a methylhydrogenpolysiloxane fluid of the general formula



in which a has a value of from 1 to 1.5, b has a value of from 0.75 to 1.25, and the sum of a and b has a value of from 2.0 to 2.25 inclusive, in an aqueous solution of a water soluble cellulose ether; said emulsion containing from 0.1 to 20 per cent by weight of the methylhydrogenpolysiloxane fluid, from 0.1 to 10 per cent by weight of the cellulose ether, and a metallic salt of a carboxylic acid.

6. The composition of claim 5 wherein the cellulose ether is selected from the groups consisting of methylcellulose and the sodium salt of carboxymethylcellulose, and the metallic salt is selected from the group consisting of the carboxylates of lead, zinc, and iron.

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No references cited.