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3,076,773

AQUEOUS EMULSION OF AN ORGANIC
SOLVENT-SILOXANE MIXTURE

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This invention relates to new and improved compositions and processes for preventing and/or minimizing adhesion of silicate adhesive compositions to heated metal surfaces, and to improvements in the preparation of corrugated board via the use of such compositions and processes.

In the manufacture of corrugated board, which term is used throughout the specification and claims to refer to the various corrugated cellulosic materials known also as boxboard, at least one planar cellulosic liner is adhesively bonded to a corrugated cellulosic element via the tips of the flutes of the corrugated element. The operations involved in manufacturing corrugated board generally comprise forming a corrugated element from so-called "corrugating material" by passing a cellulosic sheet between meshing corrugating rolls and applying an adhesive to the tips of the thus-formed flutes. Thereafter, a non-corrugated or planar cellulosic liner is applied against the adhesive-coated flutes of the corrugated element as the corrugated sheet passes between a corrugating roll and a pressure roll.

The resulting "single-faced" element may then be used as such in certain applications, but perhaps more commonly another liner subsequently is applied to the exposed corrugated side of the single-faced element in a so-called "double backing" operation wherein adhesive is applied to the still exposed tips of the flutes and a second liner sheet is applied thereagainst. The thus-formed structure is passed through a so-called "hot plate" dryer section where it is heated between a continuously moving belt and a stationary hot plate or platen surface to dehydrate the adhesive and establish an adhesive bond, the assembled structure being held in smooth contact with the hot plate by one or more steel idling rolls riding on top of the continuously moving belt.

Referring more specifically to the various operations involved in forming corrugated board, the initial bonding of a corrugated element to a liner is generally termed "single facing" and comprises adhering a corrugated cellulosic element to a flat cellulosic liner thereby to form a 2-ply structure. Such a product is known as a "single-faced" board and is typically used as such in wrapping and cushioning. In the formation of the adhesive bond in a single-facing operation, only a very short time is available for cementing the corrugated element to the flat liner as the corrugated roll and the pressure roll momentarily slam the sheets into position and apply heat and pressure to the situs of the desired adhesive bond. Typical contact times in which the adhesive bond must be formed in a single-facing operation are of the order of about $\frac{1}{50}$ to $\frac{1}{100}$ of a second. In order to form a satisfactory adhesive bond in the short time available, it is generally the practice to apply as high a pressure as possible and to operate at a relatively high temperature, the latter typically varying between about 300° and 500° F., or more, usually between 340° and 400° F. In practice, the cellulosic materials being glued frequently have a lineal speed in the range of about 300 to 500 ft. per minute so that it will be appreciated that only a small time is available for forming the desired adhesive bonds.

The other principal operation referred to hereinbefore in forming corrugated board is that of applying a second liner sheet to a single-faced corrugated element. In this

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operation, which generally is termed "double-facing" and is accomplished in a so-called "double facer" or "double backer," a previously-formed, single-faced corrugated structure comprising a flat cellulosic sheet superimposed on, and adhesively-bonded to, a corrugated, cellulosic element is provided with a second liner sheet bonded to the exposed flutes of the single-faced corrugated element.

The single-facing type of operation can be repeated as desired to form a so-called "double-walled" board comprising two flat liners and two corrugated members bonded to a third flat liner therebetween, or a so-called "triple-wall" board comprising four flat liners and three corrugated elements adhesively-bonded sandwich-style therebetween and having the same or different flute heights, e.g., so-called "A," "B" or "C" flutes, therebetween.

In forming the double-faced board in the double-backer, the problems encountered with respect to adhesive bonding are somewhat different from those involved in single-facing operations in that a longer time is available for forming the adhesive bond, typically from about 5 to 20 seconds. Also, somewhat lower machine temperatures are encountered, typical hot plate temperatures in a double-backer being within the range from about 300° to 350° F.

Difficulties in the manufacture of corrugated board arise when aqueous adhesive silicate compositions come in contact with the corrugating, pressure and idling rolls, platens of the hot plate dryers and other heated metal surfaces of the apparatus, undesirably forming glasslike, hard, adherent deposits thereon, thus fouling the rolls and hot plate sections and necessitating an interruption in production to remove the deposits. Further, as the laminated cellulosic structure passes between the belt and the stationary platens of the hot plate section, some of the adhesive silicate composition frequently exudes from the portions of the laminate nearest the edges thereof, and is deposited upon the stationary heated metal surface of the platen. After a relatively short time, these deposits of exuded silicate adhesive accumulate on the surface of the platen and other heated metal surfaces and build up into ridges or mounds near the edges of the moving laminated web and under the influence of the relatively intense heat are dehydrated to a hard, strongly adherent, solid silicate. Such hard deposits are then in a position to destroy the edges of the moving laminated structure passing across the heated surfaces.

Moreover, as the production of corrugated board of lesser and greater widths may be scheduled alternately on the same equipment during a given production period, the changeover from a lesser to a greater width may leave hard, adherent silicate deposits of the dehydrated adhesive in position to score substantial areas of the wider corrugated board being formed on such equipment. When the accumulation of the deposits of dehydrated silicate is sufficient to cause a destruction of substantial areas of the wider, laminated web passing thereover, the entire operation must be interrupted and the heated metal surfaces cleaned before the further production of such wider widths may be undertaken. A major difficulty in the cleaning operation arises in the fact that ordinarily the dehydrated silicate adheres quite strongly to the heated metal surfaces, requiring considerable time and hand labor to dislodge the deposit and refinish the surface. Accordingly, despite the many advantages of silicate adhesives, including, of course, a high degree of adhesion to cellulosic materials, one of the serious problems limiting their application heretofore has been this undesirable adhesion to heated metal surfaces.

A substantial advance in the art whereby such undesired adhesion is avoided is described and claimed in Serial No. 682,603, filed September 9, 1957, now Patent No.

3,027,291, wherein means are set forth to preclude or minimize silicate adhesion via certain silicone-containing coating compositions applied to the heated metal surfaces. While the invention described and claimed in that application is highly advantageous, it has been found that the coatings do not exhibit sufficient durability under severe use conditions in the manufacture of corrugated board and the necessary reapplication of the coatings from time to time, while effective, constitutes a problem unsolved until now.

Accordingly, the principal object of this invention is to avoid the difficulties heretofore encountered with the undesired adhesion of silicate adhesives to the platens of corrugated board manufacturing apparatus.

Another object of the invention is to provide compositions and methods for decreasing the adhesion of an aqueous adhesive silicate composition to heated metal surfaces generally.

A further object of the invention is to provide methods and compositions for preventing the adhesion of adhesive silicate compositions to stationary heated metal surfaces of corrugated board-forming apparatus.

These and other objects and advantages of the invention will appear more fully from the following description thereof.

The present invention comprises a method and composition characterized by the property of substantially eliminating adhesion of alkali metal silicate adhesives to heated metal surfaces, especially those of corrugated board manufacturing apparatus, which composition comprises, in combination, an alkyl alkoxy polysiloxane resin, a dimethyl polysiloxane and a methylhydrogensiloxane.

Such a composition when applied or present on heated metal surfaces where silicate adhesion is to be prevented produces an extremely tough, durable, highly abrasion-resistant, adherent, surface diffusion zone or coating which provides excellent anti-adhesion properties in contact with moving cellulosic corrugated board-forming elements for a much greater time than heretofore has been possible.

The proportions of alkylalkoxypolysiloxane resin, benzene-soluble dimethylpolysiloxane and methylhydrogensiloxane can be varied somewhat, the latter two ingredients usually, although not necessarily, being incorporated as a separate mixture. In general, 1 to 99 parts of the alkylalkoxypolysiloxane resin may be combined with 1 to 99 parts of the combined quantity of benzene-soluble dimethylpolysiloxane and methylhydrogensiloxane. A preferred composition range is 1 part by weight of an alkylalkoxypolysiloxane resin (100% basis) to about 4 to 12 parts of a mixture of 62 to 38% (based on siloxane content) benzene-soluble dimethylpolysiloxane and 38 to 62% (based on siloxane content) of methylhydrogensiloxane in the form of a 25% (siloxane) solution in naphtha or other solvent, a 1 to 5 ratio in terms of parts by weight of such materials being especially advantageous.

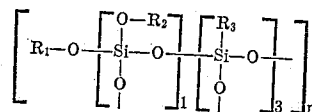
The proportions of the benzene-soluble dimethylpolysiloxane to methylhydrogensiloxane useful in the practice of this invention can be varied somewhat but it is generally desired that these two materials be employed in such proportions that the methylhydrogensiloxane comprises about 38 to 62% by weight (based upon siloxane content) while the dimethylpolysiloxane high polymer constitutes about 62 to 38% by weight (based on siloxane content).

A catalyst to facilitate heat curing of the siloxane ingredients is not essential in all instances since if a sufficient exposure to elevated temperature is possible in use, a satisfactory coating can be obtained without adding a catalyst. However, in many instances the addition of a small amount of curing catalyst to the siloxane composition is highly advantageous. Generally, thus, the amount of curing catalyst can range from 0 to about 1 part by weight of active catalyst per 1 part by weight of total silicone solids, a preferred range being about 1 part of catalyst per 2 to 200 parts of silicone solids.

Compositions of this invention as applied advantageously include a major proportion of a liquid carrier, typically an organic solvent, although in some instances water can be used with some advantage in forming aqueous emulsions, the composition and application of which will be referred to hereinafter in some detail. Such compositions in organic solvents as used exhibit stability for extended periods, e.g., 2 to 3 months or more.

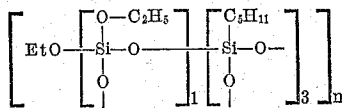
Referring more particularly to the nature of the ingredients embodied in a composition of the present invention, the expression "alkylalkoxypolysiloxane resin" refers to a petroleum oil-soluble siloxane material which has unique properties with respect to silicate adhesives in that such materials used in the practice of this invention do not adversely affect the viscosity of silicate adhesive compositions with which they may come in contact, are non-corrosive, do not have or impart an undesirable odor, are nontoxic, and do not impair the coefficient of friction of the treated metal surface, while imparting a high degree of non-adhesiveness to the treated surface.

25 An alkylalkoxypolysiloxane resin useful in the practice of this invention can be prepared by reacting an alkyl halosilane, notably, an alkyl trichlorosilane, with a poly-alkyl silicate, e.g., a tetra-alkyl silicate, and thereafter
30 hydrolyzing and at least partially condensing the resultant material to obtain a liquid, polymeric material which can be fully condensed, if desired, in a subsequent curing treatment. Alkylalkoxypolysiloxanes employed in the
35 practice of the present invention can and preferably do consist of substantially completely polymerized alkyl-polyalkoxysiloxanes, especially alkylalkoxypolysiloxanes, preferably alkylalkoxypolysiloxanes, wherein the alkyl group is selected from those hydrocarbon radicals which im-
40 part water repellency to the resultant siloxane material. Typically practicable alkyl groups are lower alkyl radicals such as butyl, amyl, hexyl, heptyl and octyl radicals; suit-
45 able alkoxy groups include methoxy, ethoxy, propoxy, and the like, groups which lead to liquid polysiloxane resins upon hydrolysis and condensation. The preferred
50 alkyl group is amyl and the preferred dialkoxy group is di-ethoxy. Hence, the specifically average preferred com-
pound of this type is amylalkoxypolysiloxane of an average molecular weight less than about 3000, e.g., as
55 prepared by conventional hydrolysis and condensation of a mixture comprising about 5 parts amyltrichlorosilane and 1 part tetraethylsilicate to obtain a product having
an ethoxy content of 9.1% by weight, a hydroxyl content of 1.5% by weight, a molecular weight of about 1200 to
60 1400 and a silanic hydrogen content of less than 0.004% by weight. The paraffin oil-soluble siloxane resin espe-
cially suited for the practice of the present invention which imparts advantageous results by way of self-releasing
65 properties is a liquid polysiloxane resin, i.e., normally liquid at room temperature, obtained by hydrolysis and
partial condensation of amylethoxysilane. Such a resin
70 can be prepared by controlling the hydrolysis and con-
densation of amyl triethoxysilane to obtain a liquid resin which can subsequently be cured, e.g., with a catalyst
such as stannous chloride because of the presence of un-
75 reacted ethoxy and/or silanol groups in the resin. The
alkylalkoxypolysiloxane to be used in the practice of this
invention has the following general structure



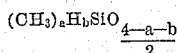
70 wherein R_1 and R_2 are the same or different lower alkyl radicals such as methyl or ethyl, R_3 is an alkyl radical or mixture of alkyl radicals, each containing from 2 to 18 carbon atoms, inclusive, and n is a number sufficient to provide an average molecular weight less than about
75 3000. Thus, the structure of the specifically preferred

amylethoxypolysiloxane compound of this type may be represented as follows:



wherein n is a number sufficient to provide an average molecular weight of less than 3000.

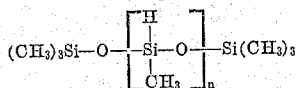
The combined methylhydrogensiloxane and benzene-soluble dimethylpolysiloxane high polymer is the material described and claimed in U.S. Patent 2,588,393—Kauppi. Thus, the methylhydrogenpolysiloxane materials are fluids in which a repeating unit ($-\text{CH}_3\text{HSiO}-$) is found. These materials may be cyclic or linear polymers end blocked with trimethylsiloxy or dimethylhydrogensiloxy units. These fluids have the general 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.

The dimethylpolysiloxane high polymers employed in the practice of the present invention are well known in the art and generally should be substantially free of $\text{Me}_3\text{SiO}_{1/2}$ and $\text{MeSiO}_{3/2}$ units. These polymers are characterized by solubility in benzene indicating substantial freedom of cross linkage and have a plasticity number of at least 30 expressed in thousandths of an inch, determined by modification of ASTM-D926-47T in which the modification is that 4.2 g. of material are used rather than the specified 2 cc., the test being conducted over a 3 minute period at 25° C. The lower plasticity number of 30 corresponds approximately to a penetrometer reading (ASTM-D217-44T) of 370 expressed in tenths of a millimeter in 10 seconds at 25° C. Dimethylpolysiloxane polymers having a plasticity number less than 110 are preferred although greater plasticity numbers may be used, as long as the polymers are substantially soluble in an organic solvent such as benzene. As used in the practice of the present invention, the mixture of soluble dimethylpolysiloxane high polymer and methylhydrogensiloxane fluid conveniently can be employed in the form of a 25% naphtha solution.

For the purposes of the present invention, a material equivalent to the described mixture of a soluble dimethylpolysiloxane high polymer and methylhydrogensiloxane fluid in the hereinbefore-indicated proportions can be obtained by mixing about 22 parts by weight of a linear methylpolysiloxane corresponding to the general formula



where n represents an integer and is at least 1, e.g., from 10 to 500 or more, the material having a viscosity-temperature coefficient of the order of 0.4 to 0.5, with about 78 parts of the hereinbefore-described mixture of methylhydrogensiloxane and dimethylsiloxane as described and claimed in U.S. Patent 2,588,393.

When a catalyst is employed, as it is in the preferred practice of the invention, the catalyst may comprise one or a mixture of several materials such as a metal salt of a carboxylic acid, e.g., a lead, iron, zinc and/or tin salt of a carboxylic acid may be used, particularly the hexoates, octoates, oleates, stearates, naphthenates, gluconates, laurates and/or resinates. In addition, copper, aluminum, manganese, cadmium, cobalt and nickel salts of carboxylic acids are useful but generally are slower acting than the lead, iron and zinc catalysts. Illustrative of

specific catalysts which may be used advantageously are lead 2-ethyl hexoate, and stannous gluconate, which is illustrative of suitable water-soluble catalysts advantageous in the preparation of aqueous emulsion compositions of this invention.

The solvent employed generally may be selected from aliphatic solvents such as kerosene, naphtha and the like, aromatic hydrocarbon solvents such as benzene, xylene, toluene or the like, and chlorinated organic solvents such as carbon tetrachloride, perchlorethylene, trichlorethylene ethylene dichloride, chlorobenzenes, and the like, the particular organic solvent being selected on the basis of cost, toxicity of the solvent vapors, solubility properties, and the like, a preferred solvent at present being perchlorethylene (tetrachlorethylene).

In some instances, the silicone materials of this invention advantageously may be combined and applied in the form of an aqueous emulsion or dispersion consisting essentially of the proportions and mixture of the hereinbefore-described silicone-containing materials with a minor amount of a wetting and/or an emulsifying agent all in an aqueous carrier, e.g., an emulsion consisting essentially of water, about 1 to 10% of the hereinbefore-described silicones, and up to about 1%, preferably about 0.01 to 0.1% of a wetting or emulsifying agent. The term "wetting agent" is intended to include both nonionic and anionic wetting agents, specific illustrative examples of which are alkyl sulphates, aromatic monosodium sulfonates derived from petroleum oils, alkyl aryl sulfonates, coconut oil sulfonates, turkey red oil, which is a sodium salt of a sulfonated castor oil, generally prepared by condensing about 4-30 mols of ethylene oxide: one mol of an alkylphenol, sodium sulfonate of petroleum hydrocarbon (C_{16}), i.e., sodium dodecyl benzene sulfonate, which typically is available commercially as a product containing 60% of sodium dodecyl benzene sulfonate and 40% of sodium sulfate, sorbitan monolaurate, Igepal CO-530 (alkyl phenoxy polyoxyethylene ethanol), polyoxyethylene sorbitan monolaurate, Igepal CO-630, and the like.

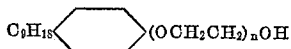
The practice of the present invention comprises applying one or a mixture of the foregoing compositions to heated metal surfaces where adhesion of alkali metal silicate adhesives is to be prevented. While the invention contemplates application of such materials to any surface in the corrugated board manufacturing apparatus, e.g., as the pressure rolls preceding the single-facing operation, corrugating rolls or other surfaces, it is especially advantageous in the treatment of the stationary, heated platens wherein the surface in operation is exposed to a rapidly-moving, relatively-abrasive cellulosic element and wherein nonadhesive properties must be achieved and maintained throughout extended periods of operation.

In the application of a composition of this invention to heated metal surfaces such as the platens, corrugating rolls, idling rolls, and the like, the coating may be applied by brushing, rubbing, swabbing, spraying, fogging, or the like, a silicone-containing solution, emulsion, suspension, dispersion or the like, subsequent heating, typically by the normally-encountered heat of the heated metal surface, to obtain a smooth and continuous coating of the silicone-containing composition on the heated metal surface. By such practice, it has been found that corrugated board can advantageously be prepared employing a conventional or an unmodified silicate adhesive, or employing and aqueous silicate adhesive composition having enhanced self-release properties. The adhesive deposits exuded on the heated metal surfaces from any silicate adhesive used are substantially entirely self-releasing for extended periods of machine operation wherein damage to the corrugated board being treated or formed is avoided without impairing the excellent and desired adhesion to cellulosic materials.

Thus, the practice of the present invention in method form comprises applying a composition hereinbefore de-

scribed to such a surface in a liquid carrier, e.g., in the form of an organic solution wherein the organic solvent is evaporated at the temperature of the metal surface, thus depositing a tough, durable, highly-adherent coating of the desired combination of silicone-containing materials in situ on the surface. Alternatively, such a protective surface diffusion zone or coating may be applied by contacting the surface with an aqueous emulsion of these materials. However, application of the aqueous emulsion alone has not been found to be the preferred practice insofar as achieving an extremely durable, protective coating is concerned. Optimum results are obtained when an aqueous emulsion is to be used if an initial treatment of the metal surface by application of an organic solution of the desired combination of silicone-containing materials is made and the solvent evaporated to obtain an initial surface coating and subsequently there is applied an aqueous emulsion of this invention from which the water is evaporated at the temperature of the metal surfaces and the silicone materials deposited as the water is eliminated.

A still more advantageous method of this invention when it is desired to employ an aqueous emulsion comprises the steps of initially applying an organic solvent-siloxane mixture of this invention to the desired metal surface maintained at a temperature within the range from about room temperature up to about 175° F., preferably 150° F., evaporating the solvent and allowing this coating to remain for about one to five minutes or while the surface is heated to a temperature of about 200° F. at which time a second organic solvent-siloxane coating is applied and the metal surface then heated to a temperature of about 300°–350° F., preferably 325° to 300° F., which typically is the operating temperature of the hot plate section or platen in the formation of corrugated board. This entire coating process can be repeated, if desired, after 12 to 24 hours and for optimum results insofar as providing an extremely durable coating is concerned should be. Thereafter, applications can be made at extended intervals, if desired. However, in many instances it is highly advantageous to employ the same mixture of siloxanes but to embody this mixture in the form of an aqueous emulsion consisting essentially of a major proportion of water with a minor proportion of the mixture of siloxane materials of the type hereinbefore described, with about 1 to 2 parts of wetting agent, preferably a nonionic wetting agent, to about 10 parts total siloxane materials as employed, typically practicable wetting agents in this application being Igepal CA-630 (isooctylphenoxypolyoxyethylene ethanol) and Igepal CO-530, a polyoxyethylated nonylphenol having the formula



In order that those skilled in the art may more completely understand the present invention and the preferred methods by which the same may be carried into effect, the following specific examples are offered.

In the following examples, the tests are conducted by applying a coating composition of this invention to a heated metal surface comprising a 6" x 6" cast iron section heated by an electrical hot plate provided with a temperature control, the temperature being maintained between 300° and 350° F. during the tests. To the thus-heated plate which is previously scoured clean of any surface film or coating is applied a sodium silicate adhesive comprising, unless otherwise indicated, a material having an $\text{Na}_2\text{O}:\text{SiO}_2$ ratio of 1:3.3, specific gravity of 40.0°–41.2° Bé., and average solids content of 37.3%. Between applications of adhesive the metal surface is rubbed with a piece of corrugated board to simulate the abrasive effect encountered at the platen surfaces during manufacture of corrugated board. Whether the adhesive sticks to the plate, is self-releasing, or must be scraped from the surface, is then observed and after the silicate film is removed, the application of adhesive is repeated.

Example 1

Using as a coating composition a mixture of 0.2% of amylethoxypolysiloxane (100% silicone oil) and 1.0% of a mixture of a soluble dimethylpolysiloxane high polymer and a methylhydrogensiloxane fluid as described and claimed in U.S. Patent 2,588,393 in the form of a 25% solution in naphtha, the composition also containing a naphtha solution of 5% lead catalyst in the form of lead 2-ethyl hexoate, the catalyst solution being in the proportion of 1 part per 4 parts of combined silicone materials, and the balance of the composition being perchlorethylene.

Sodium silicate ($1\text{Na}_2\text{O}:3.3\text{SiO}_2$ —40.0°–41.2° Bé.) is applied to the thus-treated metal surface and it is observed that complete self-release, i.e., the dried adhesive silicate or silicate-containing composition can be blown from the surface with a laboratory air hose completely or with only an occasional fragmentary area of momentary adhesion easily dislodged by touching with a spatula, to be distinguished from adhesion requiring scraping to remove, it is observed that after more than 30 repeated applications and drying or dehydration of the silicate that the surface still exhibits substantially complete self-release properties, thus evidencing an extremely durable, anti-adhesive treatment.

Example 2

The procedure of Example 1 is repeated except that the coating consists of a mixture of 0.2% by weight of amylethoxysiloxane (100% silicone oil) and 1% by weight of a 25% solution in naphtha of 0.75 part of a methylpolysiloxane as described and claimed in U.S. Patent 2,491,843, 2.55 parts of a mixture of methylhydrogensiloxane and dimethylsiloxane of the type described in U.S. Patent 2,588,393, and 2.70 parts naphtha. Sodium silicate applied to the coated metal surface self-releases for at least 38 applications of the silicate.

Example 3

The compositions of the preceding examples are re-applied to the metal platens and continued self-release is observed throughout a large number of applications of silicate adhesives, the specific numbers being respectively, 37, 37 and 36, the 1:33.3 mixture not being repeated. In this further testing, the platens are allowed to stand hot overnight and the latter portion of the tests were conducted after this extended heating period, thus demonstrating that the advantageous properties are maintained throughout extended exposure to high temperature.

Example 4

There is applied to a heated metal surface a composition consisting of 197.0 parts tetrachlorethylene, 2.0 parts of the Dow Corning silicone F-121, 0.4 part amylethoxypolysiloxane, and 0.5 part of lead 2-ethyl hexoate. This material cures in 15 to 20 minutes after being applied. Applications of a silicate adhesive consisting of 80.16 parts sodium silicate, 5.51 parts added water, 8.74 parts clay and 5.59 parts urea, exhibit repeated self-release throughout an extended series of tests.

Example 5

To illustrate the surprising increase in effectiveness of anti-adhesive properties of a heated metal surface treated in accordance with the present invention throughout an extended period of use, a series of tests are conducted using a sodium silicate adhesive containing 5.7% urea as the test adhesive. Two coatings are used—No. 1 consisting of 98.9 g. perchlorethylene, 1.0 g. of the dimethyl polysiloxanemethyl hydrogen-siloxane mixture employed in Example 1 and 0.1 g. of lead 2-ethyl hexoate as the catalyst. Coating No. 2 is a similar material to which 0.2% amylethoxypolysiloxane is added. Cast iron surfaces are coated twice, once at 175° F. and once at 200° F., the metal temperature then being raised to and main-

tained between 330°–335° F. The sodium silicate adhesive is applied repeatedly as in prior examples, the metal surfaces being maintained at the test temperature over a weekend during the experiments.

Composition No. 1 self-releases 38 times before lifting or scraping is necessary. It is then recoated and its initial self-release properties are again observed. The original application of composition No. 2 self-releases more than 125 times and continues to exhibit self-release properties at the time the test is discontinued.

The expression "alkali metal silicate" as used throughout the specification and claims will be understood to refer to silicates of the various alkali metals, i.e., sodium, potassium, lithium, rubidium and cesium, the silicates of sodium being the most common commercial adhesives.

While particular reference has been made hereinbefore to the use of compositions of this invention in the manufacture of corrugated board, it will be appreciated that such compositions will be advantageous in the treatment of other metal surfaces such as so-called "dry cans" (drying rolls or cans) in textile processing equipment, in paper producing and processing equipment and other heated metal surfaces or surfaces which are, or can be, heated to cure the compositions of this invention thereon.

It is to be understood that although the invention has been described with specific reference to particular embodiments thereof, it is not to be so limited, since changes and alterations therein may be made which are within the full intended scope of this invention as defined by the appended claims.

What is claimed is:

1. A composition for decreasing the adhesion of alkali metal silicate adhesives to heated metal surfaces which comprises, in combination,

- (1) an alkylalkoxypolysiloxane,
- (2) a methylhydrogensiloxane, and
- (3) a dimethylsiloxane.

2. A composition according to claim 1 which also contains a minor proportion of a curing catalyst for the silicone materials.

3. An aqueous emulsion comprising the composition of claim 1, a minor amount of a wetting agent and a major proportion of water.

4. A composition according to claim 1 wherein the mixture of ingredients 1, 2 and 3 comprises no more than about 1% by weight of the composition, the balance of the composition comprising a liquid carrier.

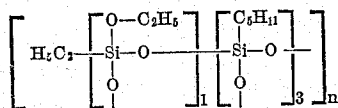
5. A composition for decreasing the adhesion of alkali metal silicate adhesives to heated metal surfaces which comprises, in combination, 1 to 99 parts of an alkylalkoxypolysiloxane, 1 to 99 parts of a mixture of methylhydrogensiloxane and dimethylsiloxane, up to 1 part of siloxane-curing catalyst per part of silicone solids, and up to 99.5 parts of added liquid carrier in addition to any solvent containing the other ingredients as incorporated.

6. A composition according to claim 5 in which the catalyst is a metal salt of a fatty acid.

7. An aqueous emulsion comprising the composition of claim 5, a minor amount of a wetting agent and a major proportion of water.

8. A composition according to claim 5 wherein the mixture of siloxane ingredients comprises no more than about 1% by weight, the balance of the composition comprising solvent.

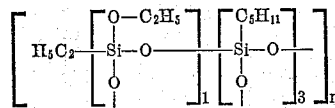
9. A composition consisting of an amylethoxypolysiloxane of the following structure



wherein n is a number sufficient to provide an average molecular weight of less than 3000; a methylhydrogen-

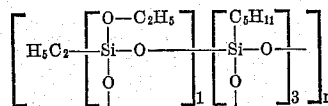
siloxane and a benzene-soluble dimethylpolysiloxane polymer; a catalytic metal salt of a carboxylic acid; and the balance a solvent.

10. A composition consisting of about 0.2% by weight of an amylethoxypolysiloxane of the following structure

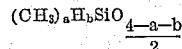


wherein n is a number sufficient to provide an average molecular weight of less than 3000; about 0.25% of a 25% solution of a mixture of methylhydrogensiloxane and a benzene-soluble dimethylpolysiloxane polymer and the balance a liquid carrier.

11. A composition consisting of a minor amount of a polysiloxane of the following structure

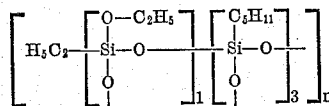


wherein n is a number sufficient to provide an average molecular weight of less than 3000; a methylhydrogensiloxane of the general formula

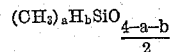


wherein a has a value from 1.0 to 1.5, inclusive, b has a value from 0.75 to 1.25, inclusive, and the sum of a and b has a value of from 2.0 to 2.55, inclusive; a benzene-soluble dimethylpolysiloxane polymer substantially free from $\text{Me}_3\text{SiO}_{1/2}$ and $\text{MeSiO}_{3/2}$ groups, and having a plasticity number of at least 30; and the balance a liquid carrier.

12. A composition consisting of a minor amount of an amylethoxypolysiloxane of the following structure

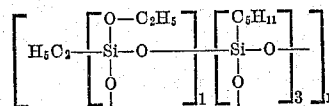


wherein n is a number sufficient to provide an average molecular weight of less than 3000; a methylhydrogensiloxane of the general formula

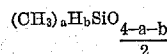


wherein a has a value from 1.0 to 1.5, inclusive, b has a value from 0.75 to 1.25, inclusive, and the sum of a and b has a value of from 2.0 to 2.55, inclusive; a benzene-soluble dimethylpolysiloxane polymer substantially free from $\text{Me}_3\text{SiO}_{1/2}$ and $\text{MeSiO}_{3/2}$ groups, and having a plasticity number of at least 30; and the balance a liquid carrier.

13. A composition consisting of 1 to 99 parts by weight of an amylethoxypolysiloxane of the following structure

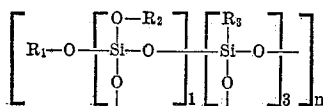


wherein n is a number sufficient to provide an average molecular weight of less than 3000; 1 to 99 parts of a mixture of 38 to 62% (based on siloxane content) of a methylhydrogen siloxane of the formula



wherein a has a value from 1.0 to 1.5, inclusive, b has a value from 0.75 to 1.25, inclusive, and the sum of a and b has a value of from 2.0 to 2.55 and 62 to 38% (based on siloxane content) of a soluble dimethylpolysiloxane high polymer having a plasticity number greater than 30;

15. A composition comprising an alkylalkoxypolysiloxane of the following structure



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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,076,773

February 5, 1963

James L. Foster et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 3, line 8, for "necesary" read -- necessary --;
column 6, line 66, for "and" read -- an --; column 7, lines
51 to 53, left-hand portion of the formula, for " C_9H_{18} " read
-- C_9H_{19} --.

Signed and sealed this 10th day of September 1963.

(SEAL)

Attest:

ERNEST W. SWIDER
Attesting Officer

DAVID L. LADD
Commissioner of Patents