United States Patent Office 3,046,155
Patented July 24, 1962

1

2

3,046,155

POLYETHYLENE-PAPER ADHESION

Lester H. Reinke, Midland, Mich., assignor to Dow Corning Corporation, Midland, Mich., a corporation of Michigan

No Drawing. Filed Oct. 6, 1960, Ser. No. 60,809
1 Claim. (Cl. 117—76)

This invention relates to an improved method for bonding polyethylene to paper.

Polyethylene-coated paper products have been used advantageously for packaging materials such as food products as well as for protective coverings for shelving and the like. The combination of paper and polyethylene has both the low-cost strength of paper and the release and partial vapor barrier properties of polyethylene. Successful bonding of polyethylene to paper has been a problem, especially with relatively non-porous papers such as glassine paper. Consequently, there has been a search for some means of satisfactorily bonding polyethylene to relatively non-porous paper as well as improving the bond of polyethylene to porous paper such as kraft paper.

The primary object of this invention is to provide a method of satisfactorily bonding polyethylene to paper. Another object of this invention is to provide such a method which requires a minimum of handling of both the paper and the polyethylene. Another object is to provide such a method involving merely surface treatment of the paper whereby a strongly-adherent hydrolytically stable coating is formed on the paper surface. These objects as well as others which are apparent from the following description are satisfied by the method of this invention.

This invention relates to a method of bonding polyethylene to paper comprising (1) treating the surface of said paper with a composition selected from the group consisting of

(A) a polyaminoalkylsilane of the formula

$$Z_nR'Si(OR)_3$$

in which each R is an alkyl radical of less than 4 carbon atoms, R′ is an aliphatic hydrocarbon radical containing a number of carbon atoms selected from the group consisting of 1 and more than 2 carbon atoms and having a valence of $n+1$ where n is a positive integer, and each Z is a monovalent radical attached to R′ by a carbon-nitrogen bond and is composed of carbon, nitrogen, and hydrogen atoms and contains at least two amine groups, the ratio of carbon atoms to nitrogen atoms in the substituent $—R'Z_n$ being less than 6:1, and

(B) soluble hydrolyzates thereof, and

(2) applying a hot polyethylene film to said treated paper surface.

In the polyaminoalkylsilanes employed in the method of this invention each R can be any alkyl radical of less than 4 carbon atoms, i.e. methyl, ethyl, propyl and isopropyl radicals. The R radicals can be the same or different. R′ can be any aliphatic hydrocarbon radical containing 1 or more than 2 carbon atoms and having a valence of at least 2, i.e. it can include in any aliphatic configuration any combination and any number of methyl, vinyl, methylene, vinylene,

$$-\overset{|}{C}H-, \text{ and } -\overset{|}{\underset{|}{C}}-$$

groups within the scope of the claim.

Each Z can be any monovalent radical attached to R′ through a carbon-nitrogen linkage, which is composed of hydrogen, carbon and nitrogen atoms, in which preferably all of the nitrogen atoms are present as amine or nitrile groups, and in which there are at least two amine groups per Z radical. The term "amine groups" comprises primary amine, secondary amine (including imine) and tertiary amine groups. The scope of Z will be better understood from a consideration of the method of producing these silanes.

The polyaminoalkylsilanes can be produced by reacting a polyamine with a halogenohydrocarbonylalkoxysilane where each halogen atom is on a carbon atom at least gamma to the silicon atom. Alternatively, they can be prepared by reacting the polyamine with an alpha-halogenohydrocarbonylalkoxysilane. In these reactions one nitrogen in the polyamine replaces a halogen atom in the halogenohydrocarbon radical, and the halogen acid is given off. The reaction is best carried out at temperatures of from 50° to 200° C. under anhydrous conditions using a molar excess of the polyamine.

The polyamines which can be employed include, for example, the following: ethylenediamine, diethylenetriamine, 1,6-hexanediamine, 3-aminoethyl-1,6-diaminohexane, N,N′-dimethylhexamethylenediamine, cadaverine, piperazine, dl-1,2-propanediamine, methylhydrazine, 1-aminoguanidine, 2-pyrazoline, benzenetriamine, benzenepentamine, benzyl-hydrazine, N-methyl-p-phenylenediamine, N,N-dimethyl-p-phenylenediamine, and 3-o-tolylenediamine.

It can be readily seen that the polyamine employed can be any aliphatic, cycloaliphatic or aromatic hydrocarbon amine containing at least two amine groups, one of which must contain at least one hydrogen atom. The term "poly" in the specification is intended to include compounds or radicals containing two or more amine groups.

The halogenohydrocarbonylsilanes employed in the above described process can themselves be prepared by the well known addition reaction of a halogenated aliphatic hydrocarbon containing at least one unsaturated carbon to carbon linkage, with a halosilane such as that of the formula $SiHX_3$ in which each X is a halogen atom, after which the addition product is alkoxylated by reacting it with one or more alcohols of the formula ROH. Examples of suitable halogenated hydrocarbons include allylbromide, allyliodide, methallylchloride, propargylchloride, 1-chloro-2-methylbutene-2, 5-bromo-pentadiene-1,3, 16-bromo-2,6-dimethylhexadecene-2, and the like. The halogenohydrocarbons can contain more than one halogen atom, as in 3,4-dibromobutene-1 and 3-chloro-2-chloromethylpropene-1, so that the radicals resulting therefrom can react with more than one amino nitrogen atom, i.e. n can be greater than 1. Preferably there should be no more than one halogen atom per carbon atom. Furthermore, no halogen atom can be so positioned that after the addition of the halogenohydrocarbon to the silicon there is a halogen atom on a carbon atom which is beta to the silicon.

A second method for preparing the halogenohydrocarbonylsilanes described above is that of halogenating an alkylhalogenosilane with elemental halogen followed by reaction with an alcohol to give the halogenohydrocarbonylalkoxysilane. This is the method employed when R′ in the above formula is a methylene radical.

The radical $(R'Z_n)$ can be of any length, so long as the ratio of carbon to nitrogen in the radical is less than 6:1. As a practical matter, the R′ radicals will ordinarily contain no more than 18 carbon atoms, and preferably contain 1 or 3 to 5 inclusive carbon atoms. The preferred Z radicals contain from 1 to 8 carbon atoms, and n is preferably 1, 2 or 3.

The polyaminoalkylsilanes can be employed by themselves but are preferably employed as from about 0.05 to about 5 percent by weight dispersions in water or an organic solvent, e.g. hydrocarbon solvents. When dispersed in water the silanes hydrolyze at least in part. When dispersed in an organic solvent or used alone the silanes can also hydrolyze to a degree dependent on the dryness of the solvent and the exposure of the silane or solution thereof to moisture, for example, from the atmosphere. Some, but probably not all, of the (OR) groups are converted to silicon-bonded (OH) groups. Some but not all of the latter then condense to form siloxane linkages. These soluble hydrolyzates of the polyaminoalkylsilanes are operative in the method of this invention and can include, for example, polymers and copolymers of units such as $Z_nR'SiO_{1.5}$, $Z_nR'Si(OH)O$, and $Z_nR'Si(OR)O$ alone or in any combination, as well as unreacted monomers and partially reacted monomers such as, for example, $Z_nR'Si(OR)_2(OH)$, $Z_nR'Si(OR)(OH)_2$, and $Z_nR'Si(OH)_3$. Such a product can be said to be one in which the polymeric units and monomeric components both fall within the formula

$$Z_nR'SiY_mO_{\frac{3-m}{2}}$$

in which R', Z and n are as defined above, m is an integer of from 0 to 3 inclusive and Y represents (OH) and/or (OR) groups where R is as defined above.

Further hydrolysis takes place when the polyaminoalkylsilanes and their hydrolyzates are applied to paper, which normally contains moisture. Subsequently, substantial condensation takes place between SiOH groups and other SiOH groups as well as SiOR groups to give a cross-linked material on the paper surface.

This paper treatment is effective on any type of paper such as glassine, parchment, kraft, tissue and the like.

The polyaminoalkylsilanes and/or soluble hydrolyzates thereof in solution or in a solvent-free state can be applied to a paper surface by any practical means such as, for example, spraying, roller-coating, brushing, dipping, Mayer rod coating and the like. Generally, the treated paper surface which is wetted by this application is allowed to dry especially where a dispersion has been used in the treatment, but drying of the treated paper is not necessary to the method of this invention where a solvent-free polyaminoalkylsilane or fluid hydrolyzate thereof is employed.

Polyethylene film is applied while hot, generally by extrusion, onto the treated paper surface. The film adheres strongly to the treated paper surface.

The following examples are illustrative only. The symbols Me and Et have been used to represent methyl and ethyl radicals respectively. The monomeric silanes employed in these examples were obtained as illustrated by the following preparations. $HSiCl_3$ and allyl chloride were reacted in the presence of chloroplatinic acid to produce $ClCH_2CH_2CH_2SiCl_3$. The latter was reacted with methanol to produce the corresponding chloropropyltrimethoxysilane, which was in turn reacted with ethylene-diamine at reflux temperature to produce $(MeO)_3Si(CH_2)_3NHCH_2CH_2NH_2$, B.P. 140.5° C. at 15 mm. Hg pressure. By mixing one mole of the $(MeO)_3Si(CH_2)_3NHCH_2CH_2NH_2$ with 3 mols of acrylonitrile, keeping the resulting exothermic reaction at about 55° C. for 1.5 hours by external cooling and then heating the mixture at 95° C. for 4 hours, and flash distilling the reaction product to a pot temperature of 168° C. at 15 mm. Hg and thus distilling off one mol of unreacted acrylonitrile, there was obtained a brown oily liquid residue consisting essentially of the compound

$$(MeO)_3Si(CH_2)_3NHCH_2CH_2N(CH_2CH_2CN)_2$$

n_D^{25} 1.4615.

Example 1

Glassine paper sheets were coated using a Mayer rod with 0.1, 0.25, 0.5 and 1 percent by weight solutions of $(MeO)_3Si(CH_2)_3NHCH_2CH_2NH_2$ in hexane. The treated surfaces of these sheets were allowed to air-dry. Hot polyethylene having a melt index of 5 and a density of 0.916 g./cc. was extruded in a thin film (from 0.5 to 1 mil) onto each of the treated paper surfaces and was allowed to cool. In every case adhesion of the polyethylene to the treated paper surface was excellent indicating the impossibility of separating the polyethylene film from the paper without destroying the film.

Example 2

Glassine paper was coated using a Mayer rod with a one percent by weight solution of a soluble hydrolyzate of redistilled $(MeO)_3Si(CH_2)_3NHCH_2CH_2NH_2$ in water. The treated paper surface was allowed to air-dry. Hot polyethylene having a melt index of 5 and a density of 0.916 g./cc. was extruded in a thin film (from 0.5 to 1 mil) onto the treated paper surface and was allowed to cool. Adhesion of the polyethylene to the treated paper surface was excellent.

Example 3

$(EtO)_3Si(CH_2)_3NHCH_2CH_2NH_2$ was substituted for the redistilled $(MeO)_3Si(CH_2)_3NHCH_2CH_2NH_2$ in Example 2. The adhesion of the polyethylene to the treated paper surface was good indicating that any attempt to separate the polyethylene film from the paper resulted primarily in destruction of the film with only rare incidence of film-paper separation.

Example 4

When $(MeO)_3Si(CH_2)_3NHCH_2CH_2N(CH_2CH_2CN)_2$,

$$(MeO)_3SiCH_2CH_2\underset{\displaystyle |\atop \displaystyle CH_2NHCH_2CH_2NH_2}{C}HNHCH_2CH_2NH_2$$

$$(MeO)_3SiCH_2NHC_6H_4NMe_2$$

$$(MeO)_3Si(CH_2)_3NH(CH_2)_6NH_2$$

$$(MeO)_3Si(CH_2)_3NHC_6H_3(NH_2)_2 \text{ and}$$

$$(MeO)_3Si(CH_2)_3NMe(CH_2)_6NHMe$$

are each substituted mol per mol for the

$$(MeO)_3Si(CH_2)_3NHCH_2CH_2NH_2$$

employed in Example 1, similar results are obtained.

That which is claimed is:

A method of bonding polyethylene to paper comprising (1) treating the surface of said paper with a composition selected from the group consisting of

(A) a polyaminoalkylsilane of the formula

$$Z_nR'Si(OR)_3$$

in which each R is an alkyl radical of less than 4 carbon atoms, R' is an aliphatic hydrocarbon radical containing a number of carbon atoms selected from the group consisting of 1 and from 3 to 18 inclusive carbon atoms and having a valence of $n+1$ where n is a positive integer ranging in value from 1 to 3 inclusive, and each Z is a monovalent radical attached to R' by a carbon-nitrogen bond and is composed of nitrogen atoms, hydrogen atoms and from one to about eight carbon atoms and contains at least two amine groups, the ratio of carbon atoms to nitrogen atoms in the substituent —$R'Z_n$ being less than 6:1, and

(B) soluble hydrolyzates thereof, and

(2) applying a hot polyethylene film to said treated paper surface.

References Cited in the file of this patent

UNITED STATES PATENTS

2,607,712	Sturken	Aug. 19, 1952
2,686,744	Cornwell	Aug. 17, 1954
2,736,721	Dexter	Feb. 28, 1956
2,971,864	Speier	Feb. 14, 1961