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3,092,594

POLYURETHANE RESIN OBTAINED FROM COAL TAR PITCH REACTION PRODUCTS AND PROCESS FOR PREPARING SAME

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This invention relates to the production of plastic materials. More particularly, this invention is concerned with improvements in the use of coal tar pitch and products obtained therefrom.

The term "coal tar pitch" as used herein is understood in the tar industry to designate a residue of coal tar distillation which is substantially insoluble in alkali, ethanol and isopropanol. The term is used in this sense in the following specification and in the claims. The term is further defined in Encyclopedia of Chemical Technology, vol. 13, page 625, published by The Interscience Encyclopedia, Inc., New York, New York, 1954, and in Asphalts and Allied Substances, Fifth Edition, vol. 1, page 59, published by Van Nostrand, 1945.

It has been proposed heretofore to prepare coatings from coal tar pitch; indeed even moldings have been prepared. The coatings are conventionally used for coating pipelines and roofing, for example. Two methods of applying these coatings are, generally used, namely, hot applied coatings and cold applied coatings. Neither method is entirely satisfactory. The hot applied coatings involve the use of a heating kettle and attendant crews. The cold applied coatings are unsatisfactory because they are slow to dry and yield only soft coatings. Where moldings have been prepared, they are very fragile and indeed this property makes them useful in the production of clay pigeons which are used as targets for trap shooting and skeet shooting. Molded clay pigeons are prepared by heating coal tar pitch with limestone dust and casting the mixture in a mold. The resulting clay pigeons are so fragile that they have no other utility. It has not been possible heretofore to use coal tar pitch in the production of more refined plastics such as foam and nonporous elastomeric products.

It is, therefore, an object of this invention to provide improved plastics which are based on coal tar pitch. Another object of this invention is to provide improved coal tar pitch coatings. A further object of the invention is to provide improved coal tar pitch moldings. Still another object of the invention is to provide cellular plastics based on coal tar pitch. Another object of the invention is to provide nonporous plastics based on coal tar pitch. A particular object of the invention is to provide coal tar pitch coatings which have improved hardness and resistance to organic solvents.

The foregoing objects and others which will become apparent from the following description are accomplished in accordance with the invention, generally speaking, by providing plastics obtained from an organic polyisocyanate and the reaction product of coal tar pitch and an alkylene oxide or alkylene carbonate. In accordance with the invention, therefore, cellular and noncellular plastics are produced by reacting coal tar pitch in a first step with an alkylene oxide or alkylene carbonate and then combining the resulting product with an organic polyisocyanate in a second step to produce the desired type of plastic. The exact nature of the reaction mechanism leading to the production of these plastics is not completely understood. However, it is believed that the alkylene oxide or alkylene carbonate reacts with reactive groups in the coal tar pitch including aliphatic hydroxyl

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groups, carboxylic acid groups, phenolic hydroxyl groups and/or amino groups to produce side chains containing terminal hydroxyl groups which will in turn react with an organic polyisocyanate to produce a polyurethane plastic.

Any suitable coal tar pitch may be used to prepare the plastics of the invention. Coal tar pitch is a complex mixture of polynuclear aromatic compounds containing phenolic groups, amino groups and other active hydrogen containing groups. The consistency of coal tar pitch may vary from that of heavy tar to that of hard pitch or semicoke. The coal tar pitch preferably has a softening point of from about 100° F. to about 300° F. The softening points referred to are determined by the ASTM standard ring and ball method D36-26 unless otherwise specified and penetration values referred to herein are determined by ASTM method D5-52. The coal tar pitch will react readily with an alkylene oxide or alkylene carbonate. The products of the reaction between the alkylene oxide and/or alkylene carbonate are hereinafter referred to as "modified coal tar pitch."

Any suitable alkylene oxide and/or alkylene carbonate may be used to modify the coal tar pitch. It is preferred that the alkylene oxides contain only one epoxy group and the use of cyclic carbonates is preferred. Therefore, suitable alkylene oxides include ethylene oxide, propylene oxide, butylene oxide, amylene oxide, styrene oxide, butadiene diepoxide, epichlorohydrin and the like. Suitable alkylene carbonates are, for example, ethylene carbonate, propylene carbonate, 1,2-butylene carbonate, 1,2-glycerine carbonate and the like. The reaction of the coal tar pitch with the alkylene oxide and/or alkylene carbonate is carried out in a straight-forward and convenient manner by simply melting the coal tar pitch and mixing it with the alkylene oxide or alkylene carbonate. The resulting mixture is then heated until the two components have become combined. Preferably, a chemical combination as set forth above is effected during this heating stage. Where alkylene carbonates are employed the reaction will be essentially complete when gas evolution ceases. The resulting product has a much lower isocyanate equivalent than the unmodified coal tar pitch. "Isocyanate equivalent" is the amount of the coal tar pitch or modified coal tar pitch in grams which will react with one mol of phenyl isocyanate. The change in the isocyanate equivalent of the coal tar pitch after it has been modified with an alkylene oxide or alkylene carbonate shows that there are very few reactive groups in the unmodified material.

The modified coal tar pitch may be reacted with any suitable organic polyisocyanate to produce either cellular or noncellular plastics as more particularly set forth below.

Suitable organic polyisocyanates include aromatic, aliphatic and heterocyclic polyisocyanates. In other words, any suitable organic radical may be bonded to a plurality of isocyanate groups to form the organic polyisocyanate used in the process of the present invention including acyclic, alicyclic, aromatic and heterocyclic radicals. Suitable organic polyisocyanates, are, therefore, ethylene diisocyanate, ethylidene diisocyanate, propylene - 1,2 - diisocyanate, cyclohexylene - 1,2 - diisocyanate, m-phenylene diisocyanate, 2,4-toluylene diisocyanate, 2,6 - toluylene diisocyanate, 3,3' - dimethyl-4,4'-biphenylene diisocyanate, 3,3'-dimethoxy-4,4'-biphenylene diisocyanate, 3,3'-diphenyl-4,4'-biphenylene diisocyanate, 4,4'-biphenylene diisocyanate, 3,3'-dichloro-4,4'-biphenylene diisocyanate, p,p',p''-triphenylmethane triisocyanate, 1,5-naphthalene diisocyanate, furfurylidene diisocyanate or polyisocyanates in a blocked or inactive form such as the bis-phenyl carbamates of 2,4- or 2,6-toluylene diisocyanate, p,p'-diphenylmethane diisocyanate, p-phen-

ylene diisocyanate, 1,5-naphthalene diisocyanate and the like. It is preferred to use the commercially available mixture of toluylene diisocyanates which contains 80 percent 2,4-toluylene diisocyanate and 20 percent 2,6-toluylene diisocyanate or 4,4'-diphenylmethane diisocyanate.

It is sometimes desirable to mix the modified coal tar pitch with other organic compounds containing at least two active hydrogen containing groups as determined by the Zerewitinoff method. Suitable organic compounds containing active hydrogen containing groups are, for example, hydroxyl polyesters, polyhydric polyalkylene ethers, polyhydric polythioethers and the like. These compounds preferably have a molecular weight between about 500 and about 10,000, most preferably between about 1,000 and about 5,000, hydroxyl numbers of about 25 to about 600 and acid numbers where applicable below about 5. Any suitable hydroxyl polyester may be used such as are obtained, for example, from polycarboxylic acids and polyhydric alcohols. Any suitable polycarboxylic acid may be used such as, for example, oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, brassylic acid, thapsic acid, maleic acid, fumaric acid, glutaconic acid, α -hydromuconic acid, β -hydromuconic acid, α -butyl- α -ethyl-glutaric acid, α - β -diethylsuccinic acid, isophthalic acid, terephthalic acid, hemilellic acid, trimellitic acid, trimesic acid, mellophanic acid, prehnitic acid, pyromellitic acid, benzene-pentacarboxylic acid, 1,4-cyclohexanedicarboxylic acid, 3,4,9,10-perylene-tetracarboxylic acid and the like. Any suitable polyhydric alcohol may be used such as, for example, ethylene glycol, 1,3-propylene glycol, 1,2-propylene glycol, 1,4-butylen glycol, 1,3-butylen glycol, 1,2-butylen glycol, 1,5-pentane diol, 1,4-pentane diol, 1,3-pentane diol, 1,6-hexane diol, 1,7-heptane diol, glycerine, trimethylol propane, 1,3,6-hexanetriol, triethanolamine, pentaerythritol, sorbitol and the like.

Any suitable polyhydric polyalkylene ether may be used such as, for example, the condensation product of an alkylene oxide or of an alkylene oxide with a polyhydric alcohol. Any suitable polyhydric alcohol may be used such as those disclosed above for use in the preparation of the hydroxyl polyesters. Any suitable alkylene oxide may be used such as, for example, ethylene oxide, propylene oxide, butylene oxide, amylene oxide and the like. Of course, the polyhydric polyalkylene ethers can be prepared from other starting materials such as, for example, tetrahydrofuran, epihalohydrins such as, for example, epichlorohydrin and the like as well as aralkylene oxides such as, for example, styrene oxide and the like. The polyhydric polyalkylene ethers may have either primary or secondary hydroxyl groups and preferably are polyhydric polyalkylene ethers prepared from alkylene oxides having from two to five carbon atoms such as, for example, polyethylene ether glycols, polybutylene ether glycols and the like. It is often advantageous to employ some trihydric or higher polyhydric alcohol in the preparation of the polyhydric polyalkylene ethers so that some branching exists in the product. Generally speaking, it is advantageous to condense from about 5 to about 30 mols of alkylene oxide per functional group of the trihydric or higher polyhydric alcohol. The polyhydric polyalkylene ethers may be prepared by any known process such as for example, the process disclosed by Wurtz in 1859 and in Encyclopedia of Chemical Technology, vol. 7, pp. 257-262, published by Interscience Publishers Inc. (1951) or in U.S. Patent 1,922,459.

Any suitable polyhydric polythioether may be used such as, for example, the condensation product of thiodiglycol or the reaction product of a polyhydric alcohol such as is disclosed above for the preparation of the hydroxyl polyesters with any other suitable thioether glycol.

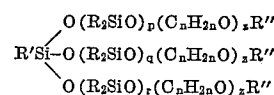
Other suitable polyhydric polythioethers are disclosed in U.S. Patents 2,862,972 and 2,900,368.

The hydroxyl polyester may also be a polyester amide such as is obtained, for example, by including some amine or amino alcohol in the reactants for the preparation of the polyesters. Thus, polyester amides may be obtained by condensing an amino alcohol such as ethanolamine with the polycarboxylic acids set forth above or they may be made using the same components that make up the hydroxyl polyester with only a portion of the components being a diamine such as ethylene diamine and the like.

In accordance with a preferred embodiment of the invention coatings are prepared by mixing the modified coal tar pitch with an organic polyisocyanate or blocked polyisocyanate such as, for example, the reaction product of 2 mols of pentanol with 1 mol of a toluylene diisocyanate, such as 2,4-toluylene diisocyanate, and applied to any suitable substrate. The coating solutions are preferably prepared in an inert organic solvent such as, for example, xylene, ethyl acetate, ethylene glycol monoethyl ether acetate and the like. Moreover, the coating compositions can be applied by any suitable method such as, for example, brushing, dipping, spraying and the like. The coating compositions are preferably applied in the above-defined inert organic solvent. Where the blocked isocyanates are used, it is necessary to heat the coating composition to release the isocyanate. For this purpose temperatures above about 300° F. are usually sufficient. The coatings obtained, however, will air dry if they are mixed with an organic polyisocyanate in a solvent and applied directly to a substrate such as metal, for example, steel, wood and the like. Moreover, the coatings obtained are hard and resistant to organic solvents while retaining the water repellency characteristic of coal tar coatings. The coatings of the invention are particularly useful for coating pipelines and for roofing and the like.

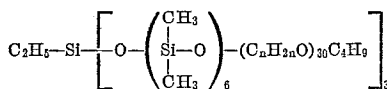
It is also possible in accordance with the invention to prepare cellular plastics. In accordance with this process the modified coal tar pitch is mixed with an organic polyisocyanate and water or a halohydrocarbon such as trichlorofluoromethane, dichlorodifluoromethane and the like and allowed to react to produce a cellular plastic. The cellular plastics of the invention are preferably prepared by combining the modified coal tar pitch with an organic polyisocyanate and water in the presence of a catalyst and a foam stabilizing agent. Any suitable catalyst may be used including, for example, tertiary amines such as, for example, triethylene diamine, N-methyl morpholine, N-ethyl morpholine, diethyl ethanalamine, N-coco morpholine, 1-methyl-4-dimethyl amino ethyl piperazine, 3-methoxy-N-dimethyl propyl amine, N-dimethyl-N'-methyl isopropyl propylene diamine, N,N-diethyl-3-diethyl amino propyl amine, dimethyl benzyl amine and the like. Other suitable catalysts are for example, tin compounds such as, stannous chloride, tin salts of carboxylic acids, such as dibutyl tin di-2-ethyl hexoate as well as other organo metallic compounds such as are disclosed in U.S. Patent 2,846,408 and in copending application S.N. 835,450.

Suitable foam stabilizers are for example, polydimethyl siloxanes or alkyl silane oxyalkylene block copolymers. The latter type of silicone oil is disclosed in U.S. Patent 2,834,748. Where polyhydric polyalkylene ethers are included in the reaction mixture to prepare a cellular polyurethane plastic, it is preferred to employ the silicone oil of the above patent which has the formula



wherein R, R' and R'' are alkyl radicals having 1 to 4 carbon atoms; p, q and r each have a value of from 4 to 8 and $(\text{C}_n\text{H}_{2n}\text{O})_z$ is a mixed polyoxyethylene oxy-

propylene group containing from 15 to 19 oxyethylene units and from 11 to 15 oxypropylene units with z equal to from about 26 to about 34. Most preferred is a compound having the formula



wherein $(\text{C}_n\text{H}_{2n}\text{O})$ is a mixed polyoxyethylene and oxypropylene block copolymer containing about 17 oxyethylene units and about 13 oxypropylene units.

The cellular plastics of the invention may be used to prepare improved sound absorbing coatings on metal, for example. Thus, they are particularly useful in the preparation of undercoatings for automobiles and the like.

It is also possible to prepare nonporous plastics from the modified coal tar pitch. The reaction leading to the production of the hard nonporous plastics is usually an exothermic reaction and the reaction product will gel in a short time to yield a hard plastic. In accordance with this process, the modified coal tar pitch is mixed with an organic polyisocyanate and cast in any suitable mold. The castings are useful as sealants and the like and are resistant to organic solvents in contrast to the unmodified coal tar pitch.

The invention is further illustrated by the following examples in which the parts are by weight unless otherwise indicated.

EXAMPLE 1

(a) About 200 grams of a coal tar pitch which is insoluble in alkali, ethanol and isopropanol and has an isocyanate equivalent of about 16,300 is combined with about 40 grams of ethylene carbonate and heated to about 200–220° C. After about 30 minutes gas evolution begins and continues for about 45 minutes when it essentially ceases. The reaction flask has lost a weight of about 23 grams; the theoretical weight loss of CO_2 is about 20 grams. A black liquid is obtained which is less viscous than the starting material. The isocyanate equivalent of the product is about 693.

(b) Example 1(a) is repeated except about 80 grams of ethylene carbonate is used. The gas evolution begins after about 30 minutes heating and continues for about 90 minutes. The weight loss is about 44 grams; the theoretical loss of CO_2 is about 40 grams. This material is less viscous than that obtained in Example 1(a). The isocyanate equivalent of the product is about 617.

(c) About 260 parts of the modified coal tar pitch as prepared in Example 1(a) is combined with about 260 parts xylene and about 350 parts of the reaction product of about 1 mol 1,3-butane diol, about 1.5 mols trimethylol propane and about 6.2 mols of a mixture of 80 percent 2,4- and 20 percent 2,6-toluylene diisocyanate in a 75 percent by weight solids solution in ethyl acetate. The resulting solution is applied to a steel panel with a doctor blade and allowed to air dry for about three days. A hard coating is obtained on the steel panel which is resistant to aromatic solvents such as toluene and will now flow at temperatures below about 350° F.

(d) Example 1(c) is repeated except the coating is baked at a temperature of about 300° F. for about 30 minutes. Similar results are obtained.

(e) Example 1(c) is repeated except the modified coal tar pitch prepared as in Example 1(b) is used. A hard coating is obtained on the steel panel which air dries in less than three days. The resulting coating is highly resistant to aromatic solvents.

EXAMPLE 2

(a) The coal tar pitches shown below in Table I are reacted with about 40 parts of ethylene carbonate per 100 parts of coal tar pitch, following the procedure of Example 1(a) except the total reaction time is about 7

hours and the temperature varies between about 170° C. and about 190° C.

Table I

Physical Properties	Coal Tar Pitch			
	RT-2	RT-6	RT-9	RT-12
Engler specific viscosity at 104° F. (40° C.)	8-13			
Engler specific viscosity at 122° F. (50° C.)		26-40		
Float test at 89.6° F. (32° C.) Seconds			120-300	
Float test at 122° F. (50° C.) Seconds				150-220
Distillation of water free material:				
Total distillate, percent by weight--				
Start to 338° F. (170° C.)	0.0-7.0	0.0-5.0	0.0-1.0	0.0-1.0
Start to 518° F. (270° C.)				
Maximum	35.0	25.0	15.0	10.0
Start to 572° F. (300° C.)				
Maximum	45.0	35.0	25.0	20.0
Residue, fusing point, ° F.	95-149	95-153	95-158	104-158
Soluble in carbon disulfide, percent (Minimum)	88	83	78	75
Water, percent by volume, Maximum	2.0	1.5	0.0	0.0

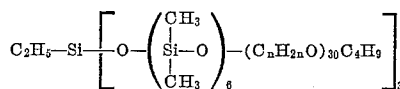
The products are black liquids which are further reacted as indicated below.

(b) About 250 parts of each of the modified coal tar pitches prepared as described in Example 1(a) are combined with about 350 parts of the reaction product of 1,4-butane diol, triethanol propane and the mixture of toluylene diisocyanates employed in Example 1(b) and 250 parts of xylene. Each of these solutions is then coated onto a steel panel and air dried for about three days. A hard coating is obtained which is resistant to organic solvents such as toluene.

(c) About 100 parts of the RT-2 ethylene carbonate condensation product prepared in Example 2(a) are combined with about 30.5 parts of a mixture of 80 percent 2,4- and 20 percent 2,6-toluylene diisocyanate. An exothermic reaction occurs immediately and the mixture gels within about one hour to yield a hard elastomeric plastic.

(d) About 100 parts of the RT-9 ethylene carbonate condensation product prepared in Example 2(a) are combined with about 150 parts of the polyisocyanate employed in Example 2(b) and heated to about 70° C. The mixture gels in about 5 minutes to yield a hard elastomeric plastic.

(e) About 50 parts of the RT-9 ethylene carbonate condensation product prepared in Example 2(a), about 50 parts of a trihydric polyalkylene ether triol obtained from condensation of propylene oxide and glycerine to a molecular weight of about 3,000 and having a hydroxyl number of about 56 are mixed and then combined with about 20 parts of a mixture of 80 percent 2,4- and 20 percent 2,6-toluylene diisocyanate, about 20 parts of trichlorofluoromethane, about 0.1 part of stannous octoate, about 0.6 part of $\text{N,N,N',N'-1,3-butane diamine}$ and about 1.5 parts of an alkyl silane oxyalkylene block copolymer having the formula



wherein $(\text{C}_n\text{H}_{2n}\text{O})$ represents about 17 oxyethylene units and about 13 oxypropylene units in a machine mixer as disclosed in U.S. Reissue Patent 24,514. A soft black cellular polyurethane plastic is obtained which has a density of about 2.0 pounds per cubic foot and is suitable for use as a sound absorbing system for sheet metal and the like.

EXAMPLE 3

About 2,000 grams of the RT-9 shown in Table I are heated until molten in a 12 liter stainless steel resin reactor equipped with baffles, a stirrer, a thermometer, a

vent and an addition line. Then about 10 grams of powdered KOH are added and the reaction mixture is heated to about 160° C. About 400 grams of propylene oxide are then added over a period of about 30 hours while maintaining the pressure in the reactor below about 15 p.s.i.g. The temperature of the reaction mixture is maintained between about 160° C. and 170° C. throughout the addition. After all the propylene oxide has been added, the heating is stopped and the reaction mixture is allowed to cool to about 100° C. Then the reaction mixture is purged with HCl to neutralize the catalyst and finally with nitrogen to remove the HCl. On cooling, a liquid product is obtained which has an isocyanate equivalent of about 550.

(b) About 250 parts of the RT-9 propylene oxide condensation product prepared as described in Example 3(a) are combined with about 350 parts of the polyisocyanate employed in Example 2(b) in about 250 parts of xylene. The solution is applied to a steel panel with a doctor blade and allowed to air dry for about 3 days. A hard coating is obtained which is resistant to organic solvents such as toluene. Similar results are obtained by baking the coating for about 30 minutes at about 250° F.

It is to be understood that any other suitable coal tar pitch, alkylene oxide or carbonate, organic polyisocyanate, catalyst, stabilizer and the like could have been used in the foregoing examples in accordance with the preceding disclosure.

Although the invention has been described in considerable detail in the foregoing, it is to be understood that such detail is solely for the purpose of illustration and that many variations can be made by those skilled in the art without departing from the spirit and scope of the invention except as set forth in the claims.

What is claimed is:

1. Plastics obtained by a process which comprises reacting an organic polyisocyanate with the reaction product of a coal tar pitch and a member selected from the group consisting of an alkylene oxide having 2 to 8 carbon atoms and an alkylene carbonate.

2. Cellular plastics obtained by a process which comprises reacting an organic polyisocyanate with the reaction product of coal tar pitch and a member selected from the group consisting of an alkylene oxide having 2 to 8 carbon atoms and an alkylene carbonate in the presence of a blowing agent.

3. A coating composition obtained by a process which comprises reacting an organic polyisocyanate with the reaction product of coal tar pitch and a member selected from the group consisting of an alkylene oxide having 2 to 8 carbon atoms and an alkylene carbonate in an inert organic solvent therefor.

4. A substantially nonporous plastic obtained by a process which comprises reacting an organic polyisocyanate with the reaction product of coal tar pitch and a member selected from the group consisting of an alkylene oxide having 2 to 8 carbon atoms and an alkylene carbonate.

5. A process for the preparation of plastics which comprises reacting coal tar pitch with a member selected from

the group consisting of an alkylene oxide having 2 to 8 carbon atoms and an alkylene carbonate in a first step and thereafter reacting the resulting product with an organic polyisocyanate.

6. A process for the preparation of a cellular plastic which comprises reacting an organic polyisocyanate with water and the reaction product of coal tar pitch and a member selected from the group consisting of an alkylene oxide having 2 to 8 carbon atoms and an alkylene carbonate.

7. A method for coating substrates which comprises mixing the reaction product of coal tar pitch and a member selected from the group consisting of an alkylene oxide having 2 to 8 carbon atoms and an alkylene carbonate with an organic polyisocyanate in an inert organic solvent therefor and applying the resulting solution to said substrate.

8. A process for the preparation of a substantially nonporous plastic which comprises mixing the reaction product of coal tar pitch and a member selected from the group consisting of an alkylene oxide having 2 to 8 carbon atoms and an alkylene carbonate with an organic polyisocyanate and casting the resulting mixture in a mold.

9. Polyurethane plastics obtained by a process which comprises reacting an organic polyisocyanate with a mixture of an organic compound containing at least two active hydrogen containing groups as determined by the Zerewitinoff method and having a molecular weight of at least about 500 and the reaction product of coal tar pitch with a member selected from the group consisting of an alkylene oxide having 2 to 8 carbon atoms and an alkylene carbonate.

10. In the preparation of coal tar coatings the improvement which comprises reacting coal tar pitch with a member selected from the group consisting of an alkylene oxide having 2 to 8 carbon atoms and an alkylene carbonate and thereafter reacting the resulting product with an organic polyisocyanate.

11. A composition prepared by a process which comprises reacting an organic polyisocyanate with the product prepared by a process which comprises reacting an alkylene oxide having 2 to 8 carbon atoms with a coal tar pitch.

12. The composition of claim 11 wherein said alkylene oxide is propylene oxide.

13. The composition of claim 11 where the reaction between said coal tar pitch and said alkylene oxide is carried out in the presence of a catalyst.

14. The composition of claim 13 wherein said catalyst is KOH.

15. The composition of claim 11 wherein said alkylene oxide has only one epoxy group.

16. The composition of claim 11 wherein said alkylene oxide is ethylene oxide.

17. The composition of claim 11 wherein said organic polyisocyanate is a toluylene diisocyanate.

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