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(21) International Application Number: PCT/US98/03960 (22) International Filing Date: - 27 February 1998 (27.02.98) (30) Priority Data: 08/807,172 27 February 1997 (27.02.97) US 08/807,664 27 February 1997 (27.02.97) US (71) Applicant: DIAMOND SEAL, INC. [US/US]; Suite B, 1290 West 2320 South, Salt Lake City, UT 84119 (US). (72) Inventors: TAYLOR, George, S.; 1935 E. Lacreata Drive, Salt Lake City, UT 84121 (US). MILLER, Joel, S.; 6514 Canyon Cove Drive, Salt Lake City, UT 84121 (US). (74) Agents: BOND, Laurence, B. et al.; Trask, Britt & Rossa, P.O. Box 2550, Salt Lake City, UT 84110 (US).		(81) Designated States: AU, CA, JP, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: GLASS COATING COMPOSITION AND METHOD OF APPLICATION (57) Abstract <p>A coating composition of an alkoxy silane reacted with the surface of a glass substrate and a cleaning composition and method for cleaning said glass area is disclosed. The coating provides water repellency, durability and ease of cleaning to a glass or other siliceous surface. The coating is formed by applying an excess of an alkoxy solution containing a sulfuric acid to a glass surface with an excess of solution being applied. Preparatory to such coating application, the glass, especially if its surface is a weathered (non-virgin) surface, is cleaned vigorously with a cleaning solution containing water, phosphoric acid, hydrofluoric acid and sulfuric acid.</p>		

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GLASS COATING COMPOSITION AND METHOD OF APPLICATION

BACKGROUND OF THE INVENTION

5 Technical Field: The instant invention relates to the formation of a protective coating on a siliceous substrate through the use of an alkoxy silane to provide a weather-resistant, easily cleaned surface.

Background Art: Various silane formulations and compositions have been utilized to provide various types of coatings upon glass or other vitreous or siliceous surfaces. In U.S. Patent 3,244,541 (Fain et al.), a dimethyl diethoxy silane is
10 disclosed as one which in conjunction with a minute amount of sulfuric acid readily forms a protective coating on a vitreous surface.

 In U.S. Patent 3,442,664 a polymeric fluorine-containing, hydrolytically-stable organo siloxane having a viscosity from 500 to 500,000 centipoise is utilized as
15 a coating composition. Earlier patents such as those to Stedman (U.S. Patent 2,923,653 and U.S. Patent 2,612,458) and Fain (U.S. Patent 2,962,390) describe various silane wax compositions. The composition utilized in Fain et al. (U.S. Patent 3,244,541) is stated to form a transparent coating but that if a significant amount of sulfuric acid, for example above 0.75 % by weight, is utilized, the coating is
20 "greasy." Apparently unknown to Fain, it has been discovered that this greasiness also occurs with formulations containing less acid under varying conditions of humidity, temperature and time.

 The work of Fain et al. does not describe the various humidity conditions under which the coating compositions of Fain et al. were applied. It has been
25 discovered that at high humidity, the problem of a greasy film is much less likely to occur. If the work of Fain et al. was done in New York, the headquarters of the corporation to which the patent is assigned, then the coatings would generally have been applied in relatively high humidity conditions.

 It has recently been found that there is less problem in obtaining a useful film
30 during application in high humidity conditions. However, application of compositions of Fain et al. in low humidity applications results in greasy films. This greasiness is extremely difficult to remove and the greasy appearance is unacceptable as a coating for glass substrates in which good optical properties are desired. Thus,

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windows of buildings cannot be properly coated unless this greasy condition is prevented from occurring.

The formation of non-greasy coatings must be obtainable with every application if a coating system is to be useful in outdoor and indoor environments where various conditions of humidity, high or low, and temperature, may be encountered. In most situations, humidity control is not possible during the coating process and may vary during the course of a day or several days where all the windows of a large building, for example, are being coated.

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DISCLOSURE OF INVENTION

The instant invention relates to alkoxy silane coating compositions and to techniques for applying an alkoxy silane coating to a vitreous or siliceous surface so that a non-greasy film is formed under any condition of humidity and is adherent to said surface. The invention further involves the determination of the proper end point at which excess coating solution is to be removed. Allowing excess solution to remain on the surface under certain humidity conditions results in the formation of an unacceptable, greasy film wherein the whole coating must be removed by time-consuming abrasion and the surface cleaned and the application technique redone.

A "greasy film" or "greasy appearing film," for purposes of this invention, is a film which exhibits tackiness, non-uniform light transmissivity and/or non-uniformity of reflected light.

The attainment of a proper coating is one which is essentially a monolayer of an alkoxy silane reacted with the vitreous substrate. The greasy condition generally occurs, it is believed, through homopolymerization of excess silane whereby a non-transparent, greasy film occurs. This homopolymerized film, as could be expected, is very difficult to remove and is unacceptable in appearance and function. The alkoxy silane film reacted with the glass is typically a clear, transparent film although it may be tinted or colored. The usual vitreous surface is glass and the film's excellent transparency is very desirable for windows, mirrors and like surfaces. The film also provides an easily cleaned surface on tile and other vitreous surfaces.

The proper end point may be detected by determining the change in viscosity of the coating by optical or other techniques described herein to determine the precise

moment when the excess coating solution must be removed. Application of the alkoxy coating without the use of a good end point determiner becomes a hit or miss proposition under various conditions of temperature, humidity, etc. resulting in unacceptable coatings and a very uneconomic process.

5 The invention, in summary, is the application of an excess amount of a silane compound having at least one reactive alkoxy site, although preferably two or three such sites, to a vitreous or siliceous substrate. The end point to be determined is when the silane compound has formed at least a complete reacted monolayer on the substrate and initial homopolymerization of the silane compound has started. At such
10 time the excess silane compound is then quickly removed so that all unreacted silane and any minor amount of homopolymerized silane material are promptly removed to provide an optical-quality layer of silane reacted with the substrate surface.

 The proper end point may be determined by regularly testing the viscosity to determine that viscosity increase which indicates the initiation of
15 homopolymerization. Also, since the film becomes greasy in appearance upon homopolymerization, the coating solution may be observed with an optical dosimeter to determine the initial light transmission reduction or light diffusion of the film so that the excess coating solution may be removed before such changes in optical properties are actually observable to the unaided eye.

20 These end point determinations are essential because the elapsed time from initial application of the coating composition at which the end point occurs will vary depending upon humidity, temperature and other conditions, including substrate conditions. The proper end point determination is one which is independent of such variables and is a rigorous technique in which a light dosimeter, viscosimeter or
25 marking and timing technique, as described hereinafter, may be used, which any trained technician could perform accurately. Any other technique is merely a hit and miss approach dependent upon the art of the application technician in having a "feel" for when a film may or may not be properly cured whereby the excess coating solution is removed at the proper time so that the reacted film is actually on the glass
30 and homopolymerization of the excess silane has not proceeded to a deleterious point.

BEST MODES FOR CARRYING OUT THE INVENTION

A transparent, weather-resistant coating of an alkoxy silane on a siliceous substrate can be reliably formed under various conditions of humidity and temperature by application techniques which include determination of the proper
5 moment when excess silane is to be removed.

Coating solutions useful in forming the weather-resistant films in the instant invention utilize an alkyl alkoxy silane, preferably a dimethyl diethoxy silane, although various other alkyl alkoxy silanes, dialkoxy and trialkoxy are useful, such as trimethyl alkoxy silane, triethyl alkoxy silane and trialkoxy silanes such as methyl or
10 ethyl triethoxy silane and the like. Preferably dialkoxy silanes are utilized. The alkoxy moiety can include methoxy, ethoxy, propoxy (any isomer), butoxy (any isomer), etc. The alkyl moiety is typically a lower alkyl group such as methyl, ethyl, propyl or butyl group. Additionally, an aryl group such as phenyl and substituted phenyl can be utilized in conjunction with or in replacement of an alkyl group.

15 The alkoxy silane is mixed with a small amount of sulfuric acid, generally from about 0.2% to 0.5% by weight sulfuric acid, although other acids may be utilized. A preferred composition has about 0.25% sulfuric acid. A coating solution is formed of the alkoxy silane and acid and thoroughly mixed generally in the absence of a humid atmosphere and stored in the absence of significant humidity. The
20 solution is very reactive with water and it is generally desirable to maintain the solution in a moisture-free environment prior to its use as a coating composition.

Siliceous surfaces such as glass to be coated are generally cleaned with alcohol and then with water. If the surface is an older, weathered surface, then a more rigorous cleaning may be required. Generally, for newer surfaces, cleaning with any
25 lower alkyl alcohol, especially denatured alcohol, and water is sufficient. Alcohol is utilized to remove any grease or organic matter. Also, it is generally desirable to hydrate the substrate to which the coating solution is to be applied before the coating process takes place. A thin coating of water molecules is generally believed to assist in the reaction of the alkoxy silane with the substrate.

30 The coating solution may be applied to the glass surface via a spraying technique, that is, application as an aerosol, or the surface may be flooded with the solution or it may be applied mechanically by application from a damp cloth or other

means. It is necessary that the solution be applied over the whole surface to be coated and be applied at a relatively uniform depth.

Once the coating solution is applied, then the coating is monitored to determine the appropriate end point at which the excess solution is to be removed.

5 Determination of the proper end point is a unique feature of the instant invention. The end point to be determined is that point when a complete continuous film of silane has reacted with the substrate. An alkoxy silane reacted with the substrate forms a transparent, durable film. However, permitting the coating solution to remain on the glass surface beyond the complete reaction of a monolayer of silane
10 compound with the glass surface can result in a deleterious film having a cloudy appearance or greasy characteristic or texture including tackiness.

The greasy condition is believed to be the result of homopolymerization of excess silane compound. This homopolymerization results in an increase in viscosity and a change in the appearance and texture of the coating. Thus, the end point is
15 determined at that point which the viscosity begins to increase or at which moment the film begins to become cloudy. This end point may be determined physically by close examination of the film with a viscosimeter or with a dosimeter. A viscosimeter determines the viscosity of the film, while a light dosimeter determines the optical qualities, that is, the cloudiness or light transmissivity of the coating.

20 As indicated elsewhere herein, the elapsed time between application of the coating solution and the moment when the excess should be wiped off will vary depending upon the temperature, humidity and other variables associated with the glass substrate and other ambient conditions. Thus, the use of a rigorous method which determines the appropriate end point, regardless of the ambient or surface
25 conditions, is essential. Monitoring of the viscosity and/or optical properties of the coating provides such a determination.

Example I

A relatively new glass substrate was coated to form an optically clear, durable coating from a dimethyl silane diethoxy solution containing 0.25% by weight sulfuric
30 acid. The glass surface was first cleaned with alcohol. The alcohol-cleaned surface may be further cleaned as necessary for new glass. The glass surface is dried with an appropriate cloth and the coating solution is applied by a spray technique to form a

continuous film of solution upon the glass. At ambient coating temperatures and moderate relative humidity, the excess solution should generally be removed in about ten to about fifty seconds after the coating solution is applied to the glass. The exact moment to remove the solution occurs when the viscosity of the solution on the glass surface increases.

In this instance the viscosity change was monitored by periodically drawing a narrow spatula 1.27 centimeters (one-half inch) wide with a square end across the liquid coating to form a channel (groove) in the liquid. The time required for the two banks of the channel to close over the channel (the channel disappears) was timed with a stop watch. From prior trial and error tests, it had been determined that the proper end point occurred when it took the channel from about three seconds to about five seconds to "heal" over. When this proper end point is determined, the excess solution is wiped off with a cotton towel and the coating surface is wiped with a cloth saturated with denatured alcohol to remove any unattached polymeric material, i.e., any greasy material. This prompt removal of excess solution provides an adherent, transparent, water-repellent coating.

Although the time between application of the coating solution to a vitreous substrate and the occurrence of the end point may vary considerably due to various conditions of humidity and temperature, the end point determination conducted as set forth in the above example will give an accurate indication of the end point and the "healing" time for a channel made with a one-half inch wide spatula will be comparable regardless of humidity or temperature. This technique depends upon the viscosity and determines the necessary end point by timing the duration required for the two walls of the channel or groove to meld together. This end point test was experimentally determined by trial and error, initially, on a number of coatings to conclude empirically what time duration was the appropriate elapsed time for "healing" of a 1.27 centimeters (one-half inch) wide channel. It was found that if the excess solution was wiped off when the channel healing time was less than about three seconds, then the resulting film was not continuous and fully formed. If the time duration was in excess of about five seconds, then the excess solution caused a film which was greasy in appearance and difficult to remove and had a tacky, unacceptable surface. When such an unsatisfactory film is formed, then the whole

coating must be removed, the glass properly cleaned to be free of dirt, grease or remaining defective film and then recoated.

Typical soda-lime-silica glass, which is the composition of most commercial and auto glass, has a surface which alters chemically and physically upon prolonged exposure to weather. Even new glass has very minute surface cracks, known as "Griffith Flaws," but the surface is otherwise virgin. Exposure to water, weather and especially urban atmosphere causes leaching of the alkali metal and alkine earth metal components from the glass. Also, "hardness" deposits and staining occur and the glass surface is no longer virgin, either physically or chemically. Cleaning such old glass surfaces with alcohol and water does not properly prepare the glass for the application of the silane coating of the instant invention.

It has been discovered that a special cleaning composition having the following composition is preferred for preparing a weathered or aged glass surface for application of a silane coating according to the instant invention:

<u>Cleaning Solution Composition</u>	<u>Preferred Composition</u>	<u>Typical Range</u>
Water	48 %	72 %-35 %
Phosphoric Acid	30 %	20 %-35 %
Hydrofluoric Acid	7 %	3 %-10 %
Sulfuric Acid	15 %	5 %-20 %

The preferred cleaning compositions may vary somewhat from the above-stated preferred composition without significant diminishment of effectiveness. For example, each ingredient may vary $\pm 5\%$ to the stated range, e.g. water may be approximately 45 %-51 %; sulfuric acid approximately 14 %-16 %, HF approximate 6.5 %-7.5 % and phosphoric acid 28.5 % to 31.5 %. The above-stated percentages are percent by weight.

Although commercial glass cleaners such as Windex may be utilized for many purposes and may be used with the silane coating composition of the instant invention, the above-identified cleaning composition has demonstrated superiority to such cleaners when such silane compositions are applied to old glass. Household glass cleaners containing ammonia or acetic acid and various detergents and water are

not satisfactory for the purpose of preparing a weathered or aged glass surface to receive a silane coating in accordance with the instant invention.

An aged glass surface may be cleansed with the cleaning composition of this invention at a wide range of temperatures. The aqueous cleaning composition may be applied by spraying, squeegeeing or wiping it on a glass surface. Generally, the cleaning composition is rubbed on the surface to force the cleaning solution into cracks, fissures and depressions in the glass. More than one application of the cleaning solution may be required for glass which is very aged or weathered.

A particularly effective way of applying the cleaning solution is by rubbing it on with a sponge having an adhesive surface.

After the aged or weathered glass has been thoroughly cleaned with the cleaning solution, the glass is flushed with water and then thoroughly dried by rubbing with a dry cloth. Substantially all traces of the cleaning solution should be removed from the glass surface. An alkoxy silane, or other appropriate silane, may then be applied to the restored glass surface in the manner described hereinabove.

A significant advantage of the instant invention is that the cleaning technique and silane coating process may be practiced upon glass structures in situ. Thus, building windows, including glass curtain walls, may be readily cleaned and coated in place. Both the inside and outside of such glass structures, including glass blocks, skylights and other architectural glass structures may be readily cleaned and coated in accordance with the instant invention. Other glass structures such as vehicle and airplane windshields and windows may be readily cleaned and coated as well as siliceous tiles, shower glass and the like.

Example II

An aged, weathered window pane of a soda-lime-silica composition was treated according to the techniques of the instant invention.

The glass surface was wiped with water to remove any easily removed surface dust and grit. The surface was then wiped thoroughly with a sponge having an abrasive surface saturated with an aqueous solution of the above identified preferred cleaning composition.

The glass surface was rubbed with the saturated abrasive sponge for about two minutes to five minutes. The glass was then flushed with water for several minutes,

wiped with a dry cloth and then flushed again before it was squeegeed or wiped dry with a dry cloth. The glass surface exhibited a brilliance which was lacking prior to its being cleaned.

Very badly weathered surfaces may also require scraping with a razor-sharp blade, e.g. a 15.24 centimeter (six-inch) wide blade, to scrape off hard water deposits which have been softened by the cleaning solution.

The cleaned glass surface was then coated with a liquid coating solution of dimethyl diethoxy silane containing about 0.25 % sulfuric acid. The silane coating solution was allowed to remain on the glass until the appropriate end point was determined. The excess coating solution was then removed by wiping with a dry cloth.

The coated glass had excellent optical qualities and exhibited good surface water repellency. The coating covered the entire glass surface and was very adherent. Vigorous rubbing with steel wool, or a similar abrasive, was required to remove the coating.

Although the instant example dealt with a soda-lime-silica glass surface, the cleaning system and the coating composition work very well on tile and other siliceous surfaces and with other glasses such as borosilicate glasses, aluminosilicate glasses, and the like.

The silane coating of the instant invention protects the glass against weathering, staining and hard water deposits for many years. Such a coating also makes the glass easy to clean. Tiles and similar materials retain their glossy appearance for a very long time when coated with a silane coating according to the instant invention.

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CLAIMSWhat is claimed is:

1. A method of applying a transparent film of a silane composition to a siliceous substrate comprising:
 - 5 1) applying an amount of a silane compound, having at least one reactive alkoxy group, and an acid to a substrate sufficient to form a coating on said substrate;
 - 2) determining the end point when said silane compound has reacted to form at least a substantially complete reacted monolayer on said surface and initial homopolymerization of said silane compound is occurring; and
 - 10 3) removing substantially all unreacted silane compound and homopolymerized silane material immediately following determination of said end point whereby a durable transparent, optical quality layer of silane compound reacted with said substrate remains.
- 15 2. The method of claim 1, wherein said end point is determined by an increase in viscosity of said film indicative of homopolymerization.
3. A method for determining the initiation of homopolymerization of a reactive silane compound in admixture with an acid on a substrate containing reactive
20 sites comprising monitoring the viscosity of a liquid film formed on said substrate by reacted silane compound and upon detecting an increase in said viscosity indicative of homopolymerization then removing excess silane compound which remains unreacted with said substrate and removing any silane homopolymers.
- 25 4. The method of claim 3, wherein the monitoring of viscosity is performed by periodically drawing a spatula of selected width across the liquid film to form a channel in said liquid film and timing the closing over of said channel, the end point of silane compound reaction with said substrate being that time which had been established as indicating the initiation of homopolymerization of said silane.

5. The method of claim 4, wherein end point is a time range of about three to about five seconds for the closing over of the channel formed by a square-end spatula having a width of 1.27 centimeters (one-half inches).

5 6. The method of claim 3 wherein said monitoring of said viscosity is performed using a viscosimeter.

7. The method of claim 3 wherein said monitoring of said viscosity is performed using an optical dosimeter to detect the initiation of reduced optical clarity
10 in said liquid film.

8. A method of applying a transparent film of a silane composition to a siliceous substrate comprising:

- 1) applying a silane compound, having at least one reactive alkoxy group, and an acid
15 mixture to a substrate in an amount sufficient to produce a coating on said substrate;
- 2) reacting said silane compound and acid mixture with said substrate to form a reacted monolayer which is at least substantially complete;
- 3) determining the end point when said silane compound and acid mixture has formed
20 said reacted monolayer on said substrate and determining initiation of homopolymerization of said silane compound by forming a channel in said silane compound and acid mixture using a member having a flat edge with a thickness dimension and determining the time lapse between formation and closure of the channel; and
- 25 4) removing substantially all of said unreacted silane compound and homopolymerized silane material following determination of homopolymerization initiation whereby a durable transparent, optical quality layer of silane compound reacted with said substrate surface remains.

30 9. The method of claim 8 wherein said thickness of said flat edge of said member is 1.27 centimeters (one-half inch) and said time lapse is between about 3 seconds to about 5 seconds.

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10. A process for applying an abrasion-resistant, water-repellent coating to a damaged siliceous surface comprising:

- a) cleaning said siliceous surface with a cleaning solution consisting of water, phosphoric acid, hydrofluoric acid and sulfuric acid;
- 5 b) flushing the cleaning solution from said siliceous surface;
- c) applying a solution of an alkoxy alkyl silane to said siliceous surface for a period of time sufficient to form a substantially continuous film of said alkoxy alkyl silane reacted to said siliceous surface; and
- 10 d) removing excess solution of alkoxy alkyl silane from said siliceous surface at the moment of determination of complete formation of said substantially continuous film to thereby provide an optical quality coating on said siliceous surface.

11. The process of claim 10, wherein said siliceous surface is a glass surface.

12. An aqueous cleaning solution for cleaning the damaged surface of a siliceous body to prepare said surface for application of an alkoxy silane coating consisting essentially of:

20	Water	~ 35 %-72 % by weight
	Phosphoric Acid	~ 35 %-20 % by weight
	Hydrofluoric Acid	~ 10 %-3 % by weight
	Sulfuric Acid	~ 20 %-5 % by weight

13. The aqueous cleaning solution of claim 12, wherein said solution comprises:

25	Water	~ 48 % by weight
	Phosphoric Acid	~ 30 % by weight
	Hydrofluoric Acid	~ 7 % by weight
30	Sulfuric Acid	~ 15 % by weight

14. The process of claim 10 wherein said water is between 37%-72% by weight of said cleaning solution, said phosphoric acid is between 20%-35% by weight of said cleaning solution, said hydrofluoric acid is between 3%-10% by weight of said cleaning solution and said sulfuric acid is between 5%-20% by weight of said cleaning solution.

15. A process for applying an abrasion-resistant, water-repellent coating to a damaged siliceous surface comprising:

- a) cleaning said siliceous surface with a cleaning solution consisting of between 35%-72% by weight of water, between 20%-35% by weight of phosphoric acid, between 3%-10% by weight of hydrofluoric acid and between 5%-20% by weight of sulfuric acid;
- b) flushing the cleaning solution from said siliceous surface;
- c) applying a solution of an alkoxy alkyl silane to said siliceous surface for a period of time sufficient to form a substantially continuous film of said alkoxy alkyl silane reacted to said siliceous surface; and
- d) removing excess unreacted alkoxy silane from said siliceous surface immediately following formation of said substantially continuous film to thereby form an optical quality coating on said siliceous surface.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US98/03960

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :B05D 5/06, 3/10; C11D 9/32, 9/34

US CL :Please See Extra Sheet.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 427/140, 165, 307, 8, 9, 167, 344, 355, 369, 358, 387, 356; 510/257, 269, 163, 179, 180, 181

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Please See Extra Sheet.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 3,448,055 A (MICKELSON ET AL) 03 June 1969 (03-06-69).	
A	US 5,567,235 A (CARSON ET AL) 22 October 1996 (22-10-96).	
A	US 5,389,496 A (CALVERT ET AL) 14 February 1995 (14-02-95).	
A	US 5,512,200 A (GARCIA) 30 April 1996 (30-04-96).	
A	US 5,578,347 A (CHAN) 26 November 96 (26-11-96).	
A	US 3,104,167 A (COTTETA) 17 September 1963 (17-09-63).	



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
A document defining the general state of the art which is not considered to be of particular relevance	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*G* document member of the same patent family
O document referring to an oral disclosure, use, exhibition or other means	
P document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

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26 MAY 1998

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US98/03960

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4,675,120 A (MARTUCCI) 23 June 1987 (23-06-87).	
A	US 5,540,946 A (DEVRIES ET AL) 30 July 1996 (30-07-96).	
A	US 3,442,664 A (HEINE) 06 May 1969 (06-05-69).	
A	US 2,962,390 A (FAIN ET AL) 29 November 1960 (29-11-60).	

INTERNATIONAL SEARCH REPORT

International application No.

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A. CLASSIFICATION OF SUBJECT MATTER:

US CL :

427/140, 165, 307, 8, 9, 167, 344, 358, 369, 387; 510/257, 269, 163, 179, 180, 181

B. FIELDS SEARCHED

Electronic data bases consulted (Name of data base and where practicable terms used):

APS, CAPLUS, JAPIO, WPIDS

clean, phosphoric, water, aqueous, hydrofluoric, sulfuric, viscosity, spatula, silane, polymerize, homopolymerize, optical, coating, monolayer, reaction