

PATENT SPECIFICATION

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(19)



(54) AQUEOUS SOLUTIONS OF ORGANOSILICON COMPOUNDS, USEFUL AS ADHESION PROMOTERS AND FOR FORMING COATINGS

(71) We, Dynamit Nobel Aktiengesellschaft, a German Company, of 521 Troisdorf, Near Cologne, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us and the method by which it is to be performed, to be particularly described in and by the following statement:-

5 This invention relates to aqueous solutions of organosilicon compounds, useful as adhesion promoters and for forming coatings. 5

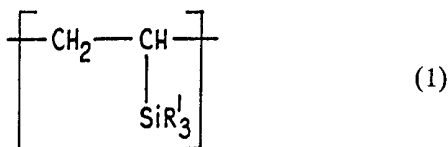
The use of organofunctional silanes as adhesion promoters between inorganic-oxidic materials and plastics materials is known. The adhesive strength thereby obtained is sufficient for many applications. However, if the adhesive bond is exposed to particular stresses, its adhesion often proves inadequate. 10

Organofunctional silanes are used also for the surface protection of inorganic-oxidic materials and metals. The use of functional-silicon silanes, for example alkyl trialkoxysilanes, is already known for this purpose. It is possible to modify the surface of the specified materials, for example inorganic pigments. For example, fluidity is improved when certain silanes are used. However, with some substrates, the application of these silanes is difficult. It is impossible for these silanes to adhere to chalk or other carbonate-containing or sulphide-containing pigments. Consequently, it was impossible hitherto to make powdered chalk water repellent by means of silanes. 15

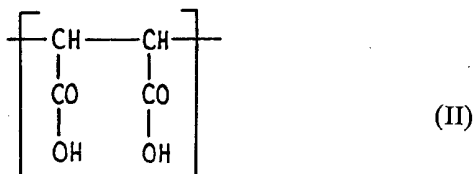
Many silane coatings hitherto applied on inorganic oxidic materials or metals have the further drawback that they are sticky, so that their fluidity is not good, i.e. they have a strong tendency to form lumps. Coatings of aminosilanes show little stickiness; however, these silanes have inadequate wettability for inorganic pigments or inorganic oxidic surfaces, with the result that they can only be supplied with advantage from organic solutions if an even coating is to be obtained. 20

Accordingly, it is desirable to find an effective substance, based on organosilicon compounds, which produces adhesion between inorganic oxidic surfaces and polymers, and which deteriorates in its adhesive effect only negligibly even under fairly strong stress, e.g. in boiling water. Furthermore, it is desirable to find a substance from which even and firmly-adhesive layers can be formed on inorganic pigments and metallic surfaces. The layers should, moreover, be hard and not sticky. 25

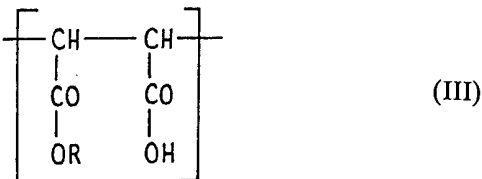
According to the present invention, there is provided a solution for improving the adhesion between an organic polymer and a metallic surface, an inorganic oxidic surface (as herein defined) or an inorganic sulphidic surface and for forming a coating on a metallic surface, an inorganic oxidic surface (as herein defined), an inorganic sulphidic surface or a plastics material surface, which solution comprises water, or a mixture of water and one or more solvents miscible therewith, having dissolved therein (a) an organosilane containing at least one hydrolysable group, and (b) a copolymer comprising (i) structural units having the general formula: 30 35



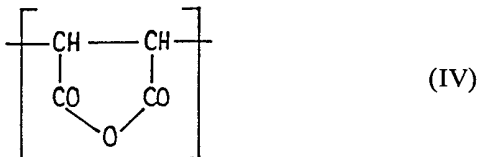
wherein R' is a radical selected from -OH and $-\left[\text{O} \right]^-$, and (ii) one or more of structural units having the general formulae:



OR



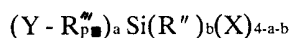
OR



wherein R is a hydrocarbyl group containing from 1 to 20 carbon atoms, the sum of the number of units of formulae (II), (III) and (IV) being not greater than the number of units of formula (I)

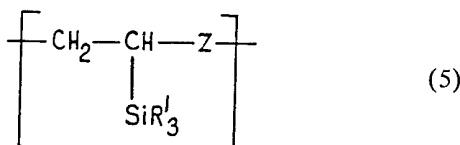
In a preferred embodiment, the invention provides aqueous solutions of organosilicon compounds characterised by a content of:

(a) a silane of the general formula:

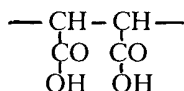


wherein a is 1 or 2 and b is 0, 1 or 2 (with the proviso that $a + b$ is not 4) and p is 0 or 1, R'' is an alkylene group containing from 1 to 8 carbon atoms or an arylene group, R' is an alkyl group containing from 1 to 4 carbon atoms or a phenyl group, X is a hydrolysable group, and Y is a functional group, a methyl group or a vinyl group; and

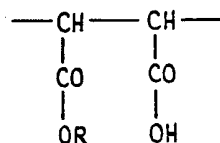
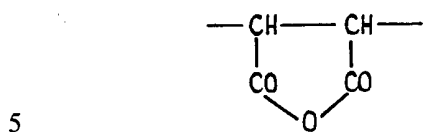
(b) copolymers with structural units of the general formula:



wherein R' is selected from -OH, $-\left[\text{O} \right]^-$, $-\left[\text{NH}_4 \right]^{++}$, $-\left[\text{O} \right]^- - \left[\text{M} \right]^+$ and $-\left[\text{O} \right]^- - \frac{1}{2} \left[\text{M}' \right]^{++}$, (wherein M is an alkali metal and M' is an alkaline earth metal) and Z is mainly a radical of the formula:



but can also be one of the radicals:



wherein R is a hydrocarbyl group containing from 1 to 20 carbon atoms.

When these solutions are used for the applications specified above, the disadvantages mentioned above of the known silanes do not occur, or only to a lesser extent. The adhesion under stress between inorganic oxidic materials and polymers is improved with the result that even in boiling water, for example, the adhesive bond obtained with the aid of the solution according to the invention has mechanical strength values which are usually higher by more than 10% than those obtained when one component contained in the solution is used alone. The adhesion promoting effect is therefore not an additive effect of the individual components, but a synergistic effect resulting from unforeseeable interactions between the individual components.

By use of the solutions according to the invention, it is further possible to apply hard, even, non-sticky coatings on inorganic oxidic materials or metals. What is particularly surprising is the fact that with the solutions of the invention, chalk is successfully made water repellent for the first time, with the result that processing of this material, e.g. to form fillers, is considerably improved.

The above-mentioned synergism occurs in this application also. The mutual influence of the components of the solution is independent of the silane used. The synergistic effect, both in the case of organofunctional silanes and in the case of functional-silicon silanes, is obtained only when the specified copolymers are used. The type of functional group or hydrocarbon residue on the silicon atom is of only secondary importance.

The preferred silanes used to produce the solutions according to the invention have the general formula given above. In this formula, a is 1, 2 or 3 and b is 0, 1 or 2, with the proviso that $a + b$ must not be 4. This proviso is essential to the invention as at least one hydrolysable radical X per molecule must be present. This hydrolysable radical can be a halogen atom, preferably chlorine, or an alkoxy group the alkyl portion of which has 1 to 8 carbon atoms, preferably 1 to 4 carbon atoms, which may be interrupted, if desired, by one or more -O- linkages. A part of this hydrolysable group may also be present in the aqueous solution as silanol radical or a silanolate radical depending on the pH of the solution.

The radical R'' in the formula for the silanes is an alkylene radical having 1 to 8, preferably 1 to 3, carbon atoms, or an arylene radical. If desired, this radical may be branched. In general, only a radical of this type is present between the silicon and the functional group, i.e. p is then 1. When radical Y is for example a $\text{CH}_2\text{CH-}$ group, as in vinyl trialkoxysilanes for instance, p can be 0.

Radical Y is a functional group or a methyl group. In the latter case, the silanes used are functional-silicon silanes in which, on the silicon, there is at least one functional group (the hydrolysable radical X) and at least one alkyl group.

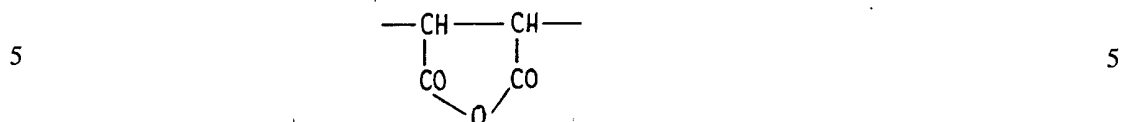
By a functional group is meant the group $\text{CH}_2 = \text{CH-}$ and any radical which can enter into reactions known *per se* with other functional groups. Examples of such radicals are amino groups, imino groups, carbonyl groups, carboxy groups, isocyanate groups, isothiocyanate groups and groups containing epoxy groups.

Examples of silanes which can be used according to the invention are: β -aminoethyl triethoxysilane, δ -aminobutyl trimethoxysilane, γ -aminopropyl trimethoxysilane, β -aminoethyl- γ -aminopropyl trimethoxysilane, α -methyl- β -aminoethyl triethoxysilane, N-dimethyl- γ -aminopropyl triethoxysilane, γ -glycidyloxypropyl trimethoxysilane, γ -glycidyloxypropyl tributoxysilane, β -3,4-epoxycyclohexylethyl trimethoxysilane, γ -mercaptopropyl trimethoxysilane, β -mercaptoethyl triethoxysilane and γ -methacryloxypropyl trimethoxysilane.

This list shows that there can be used aminosilanes in which one or both hydrogen atoms of the amino group can be replaced by a lower alkyl group, preferably with 1 to 4 carbon atoms, or by an aminoalkyl radical, e.g. an aminoethyl radical. In the case of radicals containing an epoxy group, the epoxy group is attached to the alkylene sylyl group by, for example, an ether group, e.g. the group $-\text{CH}_2\text{O-}$ or an ester group, e.g. the group $-\text{CH}_2\text{O-CO-O-}$. However, another possibility is that they are attached to the alkylene group directly or via a cycloaliphatic ring or that it is a component of a cycloaliphatic group of this type. The production of such silanes is described in Federal German Patent No. 1,061,321.

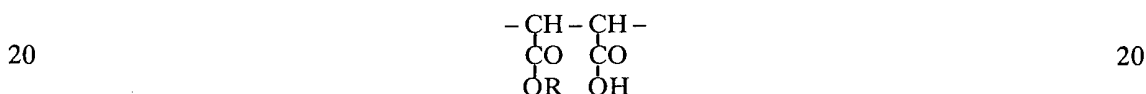
Some of the copolymers contained in the solution are known, as regards their structural

units. Compounds in which the radical Z in the structural unit stated above is a maleic acid anhydride unit:



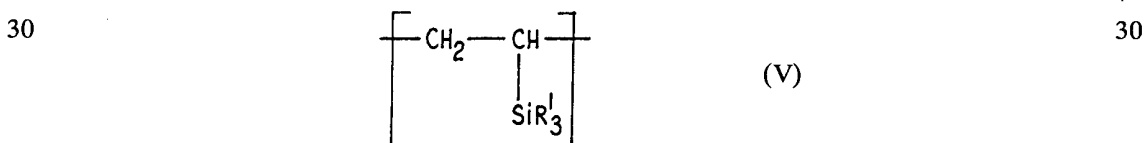
have been known for some time. They are produced by, for example, reacting maleic acid anhydride with vinyl trialkoxysilane in a molar ratio of 1:1 to 1:3 in the presence of radical-forming catalysts at temperatures between 120°C and 160°C. Organic peroxides are the preferred radical-forming catalysts, examples being benzoyl peroxide, di-tert. butyl peroxide and dicumyl peroxide. This manner of preparation is described in Ind. & Eng. Chem 45 (1953) No. 2, pages 367 to 374.

In the case of copolymers in which the radical Z in the above formula is a maleic acid ester residue:

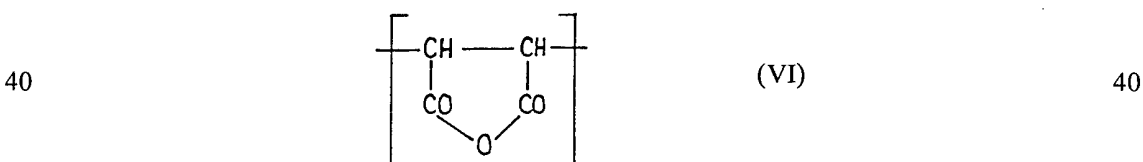


such copolymers can be obtained by dissolving the copolymers obtained according to the above reaction in an alcohol. Suitable alcohols are those with 1 to 20 carbon atoms, particularly those with 1 to 4 carbon atoms. The radical R then corresponds to the hydrocarbyl radical of the alcohol used as solvent.

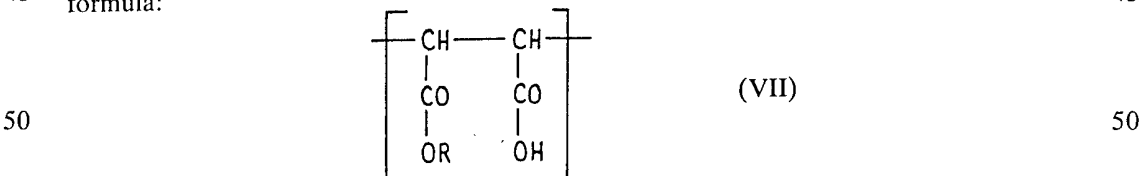
Examples of copolymers suitable for use in the invention are copolymers comprising structural units having the general formula:



and structural units having the general formula:



modified in that from 50 to 100% of the latter units are replaced by units having the general formula:



wherein R and R' are as defined above, the sum of the number of units of formula (VI) and (VII) being not greater than the number of units of formula (V). Such copolymers, amongst others, are described and claimed in Application No. 15551/78. (Serial No. 1584634)

Preferred copolymers are those wherein R is a straight-chain or branch-chain alkyl group containing from 1 to 20 carbon atoms, wherein R is an unsaturated hydrocarbyl group containing from 3 to 11 carbon atoms, and wherein R is a cycloaliphatic group containing 6, 7 or 8 carbon atoms.

As described in Application No. 15551/78, these copolymers may be produced by reacting a copolymer of a vinyl trialkoxysilane and maleic anhydride with an alcohol having the general formula ROH wherein R is as defined above, and by hydrolysing the alkoxy groups of the reaction product.

Copolymers of vinyl trialkoxysilanes and maleic anhydrides are known. They are produced by polymerisation of vinyl trialkoxysilanes and maleic anhydride in the presence of organic peroxides at temperatures between 90 and 150°C. The alkoxy group of the vinyl trialkoxysilane may have 1 to 8 carbon atoms and possibly be interrupted by an -O- radical such as in the case of vinyl tris-(β-methoxyethoxy)-silane, for example. One of the alkoxy groups may be replaced by a hydroxy group, a C₁₋₄ alkyl group or a phenyl group. The production of these copolymers is described in, for example, U.S. Patent No. 3,560,589. According to this patent, these copolymers are suitable as adhesion promoters between epoxy resins and inorganic fillers.

As described in Application No. 15551/78, (Serial No. 1584634) we have now found that the half esters deriving from these copolymers have new, unexpected properties which the known copolymers do not have or only have to a hitherto unknown small extent. These half esters may further be hydrolysed into hitherto unknown hydrolysates.

In the new vinyl trialkoxysilane/maleic anhydride half ester copolymers, the proportion of maleic acid half ester units is equal to or greater than that of the maleic anhydride units. If the reaction is conducted appropriately, it is also possible for the maleic anhydride proportion to become virtually nil.

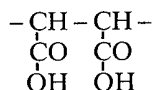
The individual copolymer units alternate in irregular sequence along the copolymer chain. The maximum sum of the maleic anhydride and maleic acid half ester units is just as great as the vinyl trialkoxysilane units. In general, the excess of vinyl trialkoxysilane units is from 0.1 to 10%. It is also possible, however, for the excess to be greater if during the production of the vinyl trialkoxysilane/maleic anhydride copolymer used as starting material, a suitable excess of vinyl trialkoxysilane is used.

The new vinyl trialkoxysilane/maleic acid half ester copolymers are produced by esterification of the maleic anhydride component of vinyl trialkoxysilane/maleic anhydride copolymers with the alcohol ROH. Esterification may take place at temperatures between 40 and 150°C, preferably between 60 and 110°C. The longer heating is conducted, the higher is the degree of esterification. The degree of esterification may also be raised by raising the temperature and particularly by adding catalysts, e.g. sulphonic acids.

If the alcohol used in the esterification is liquid, esterification expediently takes place under reflux until reflux no longer occurs. Heating can then be continued further, possibly at raised temperatures and pressure.

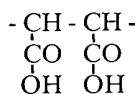
Esterification takes place both with saturated and unsaturated or cycloaliphatic alcohols. The carbon atom content of the alcohol is from 1 to 20 carbon atoms. Examples of suitable alcohols are methyl alcohol, ethyl alcohol, octyl alcohol, 2-ethyl-1-hexanol, cetyl alcohol, allyl alcohol, crotyl alcohol and cyclohexyl alcohol.

The new vinyl trialkoxysilane/maleic acid half ester copolymers are soluble in organic solvents such as alcohols or ketones (e.g. acetone). They react with water producing hydrolysates, the alkoxy groups of the silyl units being dissociated to form hydroxyl groups. Cross-linking, possibly with the formation of a -Si-O-Si- bond, with a further silyl unit to form siloxanes may then take place. During hydrolysis, the maleic acid half ester units and the maleic anhydride units react completely or partially, forming maleic acid units of the formula:

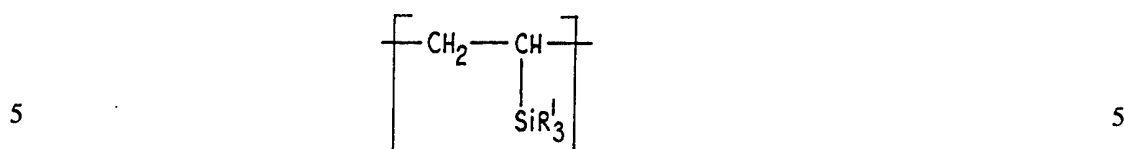


These hydrolysates are soluble in dilute alkalis. As soon as a solution has formed, the solutions may be diluted in water without a deposit being precipitated. Dilution with weak acids is also possible after formation of the solution.

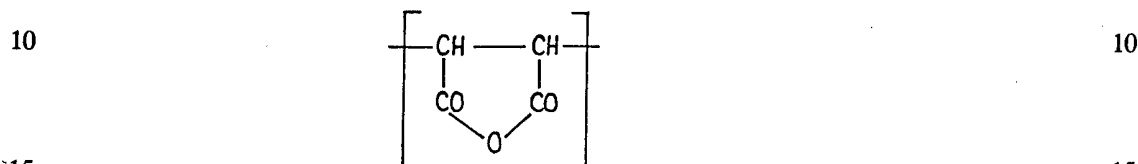
Preferred copolymers of the solutions of the invention are those in which the structural unit Z is mainly the structural unit:



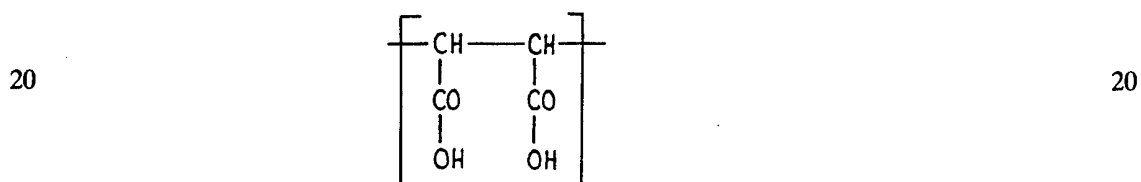
Copolymers which possess this structural unit predominantly can be produced by precipitating out of the solution of the known copolymer, produced by reaction of a vinyl trialkoxysilane with maleic acid anhydride, by addition of water, a compound insoluble in water in which the structural units are mainly (a) units having the formula:



and (b) either units having the formula:



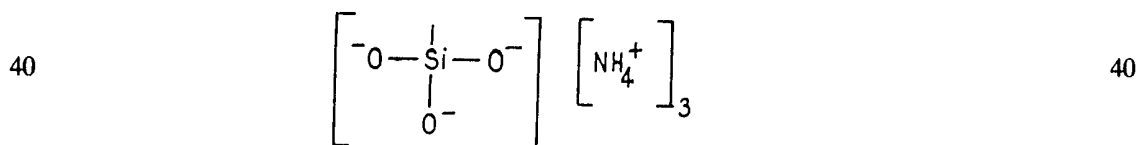
or units having the formula:



In the first formula R' is either a hydroxyl group or an oxygen bridge to a further structural unit. In the latter case, the insoluble compound contains silanol units or siloxane units as well as the maleic acid or maleic acid anhydride units.

The siloxane units of the copolymer insoluble in water, via which the individual structural units are cross-linked together, are easily broken by means of dilute alkalis. The copolymer is thereby made water-soluble again and contains the structural units specified above.

As a preference, as the alkali, there is used an aqueous ammonia solution whose NH_3 content can vary within wide limits depending in which pH range the solution obtained is to be used. In general, however, 0.5 to 5% aqueous solutions of ammonia in water are quite sufficient to produce 15 to 20% aqueous solutions of the copolymer. The silicon-containing radical in these solutions is either a silanol radical or silanolate radical having the ideal formula:



Instead of aqueous ammonia solutions, other basic aqueous solutions may also be used to break the siloxane bond in the water-insoluble copolymer and thus to produce the solution according to the invention. Possible examples are alkali metal or alkaline-earth metal hydroxide solutions, quarternary ammonia compounds or water soluble amines, for example n-amylamine, di-n-propylamine, triethylamine, ethanolamine, diethanolamine, triethanolamine or tetraalkyl ammonium hydroxides whose alkyl group has 1 to 3 carbon atoms.

In order to produce the solutions according to the invention, the solutions of the water insoluble copolymer with the siloxane and maleic acid/maleic acid anhydride units are mixed with the silanes. The silanes in this case may be used as such in solid form. However, aqueous solutions of the silanes or solutions of the silanes in a solvent mixable with water (e.g. ethanol) may also be mixed with the copolymer solution.

Since the copolymer solution has a pH above 7, stable alkaline solutions are always obtained by this manner of production. The solutions of the invention, however, are also stable at room temperature in the weakly acidic range with the result that by adding dilute acid it is possible to adjust them to any optional pH value over 3 without the solutions varying substantially in their composition. With pH values below 3, cross-linking may take place, depending on the selected concentration. This is also possible at pH values between 3 and 6, when concentrated solutions are kept for some time in this pH range. In general, therefore, the mixture is brought to the desired pH after the two components have been

mixed. But it is also possible to adjust the pH of one or both components before mixing.

The concentration of the individual components in the solution may vary within wide limits. The copolymers are preferably present in the solution in an amount of from 0.001 to 50% by weight, more preferably from 0.01 to 20% by weight. The silane component is preferably present in an amount of from 0.001 to 80% by weight, more preferably from 0.01 to 60% by weight.

The ratio of silane: copolymer is optional. The synergistic effect takes place at any ratio. It is advisable, however, for one of the two components to constitute at least 2% by weight of the dissolved organosilicon compounds.

By aqueous solutions are meant, in the present invention, solutions which may contain additionally other organic solvents miscible with water. The amount of the solvent additionally present may be greater than the amount of water. The ratio of organic solvent: water should, however, be a maximum of 2:1. A preferred additional solvent is ethanol.

As specified above, the solutions according to the invention are suitable for producing coatings on inorganic surfaces and as adhesion promoters between organic polymers and inorganic oxidic or sulphidic surfaces.

The inorganic materials on which the solutions according to the invention produce firmly adhesive, scratch resistant coatings include metals, e.g. iron, zinc, aluminium, magnesium and copper, and alloys of these metals with one another or with other metals.

By inorganic oxidic substances are meant, in the present invention, solid substances which contain oxygen in combined form, for example metal oxides, mixed oxides, carbonates, sulphates, silicates and phosphates. Examples of such substances are aluminium oxide, kaolin, clay, bauxite, silicon oxide, sand, titanium dioxide, zinc oxide, iron oxide, chromium dioxide, manganese dioxide, calcium oxide, calcium carbonate, gypsum, heavy spar, chalk, glass in all its processing forms such as threads, fibres, balls and plates.

With the solutions according to the invention, coatings may also be applied on sulphidic materials. These materials include mainly metal sulphides as occur either naturally as minerals, or as are used in the form of synthetic substances, chiefly as pigments. Examples are molybdenum sulphide, cadmium sulphide and antimony sulphide.

To produce coatings with the solutions according to the invention, there are preferably used as 0.5 to 10% by weight solutions. These solutions are applied on to the grease-free surfaces by methods known per se, for instance, by immersing, spraying, brushing or painting. The solvent is then evaporated. This may take place both at room temperature or at raised temperatures, e.g. up to about 200°C.

If the solutions according to the invention are used as adhesion promoters, they are applied in like manner to the substrate. For this purpose, however, solutions with a content of 0.05 to 2% by weight of organosilicon compounds are quite sufficient.

When used as adhesion promoter for polymers, the solution according to the invention may also be mixed into the polymer and this mixture be bonded to the inorganic oxidic material in a manner known per se. In this case, 0.5 to 5% solutions are preferably used.

The polymers which, with the aid of the solutions according to the invention, are bonded to inorganic oxidic material or metals, include both thermosetting materials and thermoplastic materials. Examples of thermosetting materials are epoxy resins, phenolic resins, unsaturated polyester resins. Examples of thermoplastic materials are polyolefins, polyamides, polycarbonates and polyesters, e.g. polytetramethylene glycolphthalate, polystyrol and polyvinyl chloride.

The invention, and the preparation of copolymers which can be hydrolysed to produce hydrolysates for use in the invention, will now be illustrated by the following Examples. The words "Araldite", "Palatal", "Omya" and "Millicarb" used in the Examples are registered Trade Marks.

EXAMPLE 1

In a three-necked flask equipped with a stirrer, an inlet tube for nitrogen and a reflux condenser having a calcium chloride tube, 147g of maleic acid anhydride were dissolved at 70°C in 510g of vinyl triethoxysilane with stirring under a nitrogen atmosphere. When a solution had been produced, 3.9g of dicumyl peroxide were added and the temperature was raised to 130°C. At this temperature, the reaction commenced. The heat of polymerisation was removed by cooling so that the temperature in the flask was between 130 and 150°C. When the reaction had subsided, stirring was continued for a further 3 hours at 130°C and the reaction was terminated.

Surplus vinyl triethoxysilane was first removed under a water jet vacuum at 60°C and then at a temperature rising to 130°C. The residual monomer was removed under an oil pump vacuum (0.1 mm Hg), and 480g of a solid, slightly yellow resin were obtained. The ratio of vinyl triethoxy units to maleic acid anhydride units in this product was greater than

1, i.e. approximately 1.1.

The copolymer was dissolved at 76°C in 500 cc of absolute ethanol. The solution was then added to 5 litres of desalted water with vigorous stirring. A fine white powder precipitated in a yield of 350g. The powder was isolated from the aqueous phase by filtering or centrifuging. It was washed and then dried in a circulating drier cabinet at 50°C. The copolymer contained maleic acid units, maleic acid monoester units, maleic acid anhydride units, vinyl silanol units and vinyl siloxane units.

One part of the solid white copolymer obtained was stirred at room temperature into 9 parts of a 1% aqueous ammonia solution. In the course of 24 hours, a clear solution was obtained.

2 parts of isobutyl trimethoxysilane were dissolved in 98 parts of a mixture of 60 parts of ethanol and 40 parts of demineralised water. A quantity of 5 ml of this silane solution was placed on a 10 x 15 cm glass plate. The plate was left to stand at room temperature, during which time the solvent evaporated. In the same way, glass plates were treated as comparison with 2% alcoholic solutions of vinyl trimethoxysilane, γ -chloropropyl trimethoxysilane, γ -aminopropyl triethoxysilane, γ -methacryloxypropyl trimethoxysilane and γ -glycidyloxypropyl trimethoxysilane, and with the clear, copolymer solution described above (after dilution to a solids content of 2% by addition of demineralised water). The results are summarised in Table 1 below.

Further solutions of the above mentioned silanes and the clear, copolymer solution were produced, these solutions containing 98 parts of a solvent mixture of 60 parts ethanol and 40 parts demineralised water and 1 part by weight of each of the silane and the copolymer. These solutions were placed on to glass plates in a similar manner as the comparison solutions. The following Table 1 gives the results of the experiments. Evaluation was made of the wetting of the glass plate by the silane solution and of the adhesion and surface quality of the film formed after evaporation of the solvent.

TABLE 1

30	Isobutyl trimethoxysilane	Wetting	Adhesion	Surface	30
	Vinyl trimethoxysilane	poor	poor	soft, sticky	
		poor	good	hard, not	
35	γ -chloropropyl trimethoxysilane	poor	good	sticky	35
	γ -aminopropyl triethoxysilane	poor	very good	soft, sticky	
				hard, not	
				sticky	
	γ -methacryloxypropyl trimethoxy				
	silane	poor	poor	soft, sticky	
40	γ -glycidyloxypropyl trimethoxy-				40
	silane	good	poor	sticky	
	Clear, copolymer solution	very good	fairly	hard, not	
			good	sticky	
	Isobutyl trimethoxysilane/	very good	very good	hard, not	
45	clear copolymer solution			sticky	45
	Vinyl trimethoxysilane/			hard, not	
	clear copolymer solution	very good	good	sticky	
	γ -chloropropyl trimethoxysilane/	very good	good	hard, not	
	clear, copolymer solution			sticky	
50	γ -aminopropyl trimethoxysilane/	good	good	hard, not	50
	clear, copolymer solution			sticky	
	γ -methacryloxypropyl trimethoxy-	good	good	hard, not	
	silane/ clear, copolymer solution			sticky	
	γ -glycidyloxypropyl trimethoxy	good	good	hard, not	
55	silane/ clear, copolymer solution			sticky	55

EXAMPLE 2

The 10% clear, copolymer solution produced according to Example 1 was diluted with demineralised water to form a 0.25% solution. Strands of water-smoothed glass fibres were immersed into this solution and then dried first at room temperature and then at 120°C. The glass fibre strands thus pretreated were then immersed in an epoxy resin mixture consisting of 55.2 parts epoxy resin, namely Araldite FRL, 44.2 parts of amine hardener, namely HT 907, and 0.6 parts of accelerator, namely DY 061, (all manufactured by Ciba Geigy AG., Basel), or in an unsaturated polyester resin (Palatal P6 manufactured by BASF,

Ludwigshafen), to which 2% by weight of dibenzoyl peroxide had been added, to form round, glass-fibre-reinforced resin bars. Hardening of the bars took place at 130°C (epoxy resin) or 100°C (polyester resin) over a period of 17 hours altogether (two hours prehardening, 15 hours after-hardening). The bending strength of these bars was then measured without moisture stress and after 72 hours in boiling water.

Round glass-fibre-reinforced bars were produced in the same way using 0.25% aqueous solutions of the adhesion promoters 2 to 5 below and their bending strengths were measured. The solutions were produced by combining 0.25% aqueous solutions of the adhesion promoters in the given ratio. The results of the measurements are summarised in Table 2.

Adhesion promoter 1 : copolymer according to Example 1

Adhesion promoter 2 : γ -aminopropyl triethoxysilane

Adhesion promoter 3 : mixture of 1 part adhesion promoter 1 and 1 part adhesion promoter 2

Adhesion promoter 4 : γ -methacryloxypropyl trimethoxysilane

Adhesion promoter 5 : mixture of 1 part adhesion promoter 1 and 9 parts adhesion promoter 4

TABLE 2

Adhesion promoter	Resin	Bending strength (kp/cm ²)	
		unstressed	72 hours in boiling water
1	epoxy	10,400	6,100
2	epoxy	11,400	8,700
3	epoxy	11,700	9,700
1	unsaturated	8,700	2,100
4	polyester	12,300	6,500
5	unsaturated	12,300	7,400
	polyester		

EXAMPLE 3

Round glass-fibre-reinforced epoxy resin bars similar to those of Example 2 were prepared using 0.25% aqueous solutions of adhesion promoters 1 to 7.

Adhesion promoter 1 : γ -aminopropyl triethoxysilane

Adhesion promoter 2 : copolymer according to Example 1

Adhesion promoter 3 : mixture of 9 parts adhesion promoter 1 + 1 part of adhesion promoter 2

Adhesion promoter 4 : mixture of 7 parts adhesion promoter 1 + 3 parts adhesion promoter 2

Adhesion promoter 5 : mixture of 5 parts adhesion promoter 1 + 5 parts of adhesion promoter 2

Adhesion promoter 6 : mixture of 3 parts adhesion promoter 1 + 7 parts adhesion promoter 2

Adhesion promoter 7 : mixture of 1 part adhesion promoter 1 + 9 parts adhesion promoter 2

The bending strengths of the bars were as given in the following Table 3.

TABLE 3

Adhesion Promoter		Bending Strength (kp/cm ²)	
		unstressed	72 hours in boiling water
5	1	11,400	8,700
	2	10,400	6,100
	3	10,200	9,400
	4	10,600	9,500
10	5	11,700	9,700
	6	11,700	9,700
	7	10,600	9,300

EXAMPLE 4

Round glass-fibre-reinforced epoxy resin bars similar to those of Example 2 were prepared using a 0.25% solution of a mixture of 1 part copolymer according to Example 1 and 1 part γ -aminopropyl trimethoxysilane. The glass fibre strands were either immersed into the freshly prepared solution or, in a second test, 48 hours after production of the solution, they were immersed into it. The determined bending strengths are given in Table 4. They show that, even after a fairly long standing period, the solutions according to the invention do not deteriorate in their effect, or at least only negligibly so.

TABLE 4

Standing time of solution (hours)		Bending strength (kp/cm ²)	
		unstressed	72 hours in boiling water
30	0	9,300	8,900
	48	10,900	8,400

EXAMPLE 5

Round glass-fibre-reinforced unsaturated polyester resin bars as in Example 2 were prepared using, as an adhesion promoter, a 0.25% aqueous γ -methacryloxypropyl trimethoxysilane solution of pH 4 and a 0.25% aqueous copolymer solution as described in Example 2. The glass fibre strands were immersed either into the freshly prepared solution or, in a second test, into the solution, 48 hours after its preparation. The pH of the adhesion promoter solution was adjusted by acetic acid to the value given in Table 5. The bars had the bending strengths given in Table 5.

TABLE 5

Standing time of the adhesion promoter solution in hours		pH of the adhesion promoter solution	Bending Strength (kp/cm ²)	
			unstr.	72 h boiling water
50	0	4	11,500	4,200
	48	4	11,400	4,900
	0	5	11,600	5,200
55	48	5	11,600	5,800
	0	6	11,600	5,400
	48	6	11,500	5,500

The Table shows that in this case, too, when the solution according to the invention is left to stand for some time, there is virtually no deterioration in the adhesion promoting effect. Moreover, when using solutions which contain methacryloxyalkyl trialkoxysilanes as their silane component to improve the adhesion between thermosetting resins and inorganic oxidic substances, it is advisable to use the solution at a pH between 4 and 6.

EXAMPLE 6

0.5 parts of propyl trimethoxysilane in the form of a 10% alcoholic-aqueous solution (alcohol : water ratio 1 : 1) were applied to 100 parts of Omya chalk, Millicarb type, by intensive intermixing in a Braun High Speed Mixer, MX 32 type. The chalk thus pretreated was then dried for 1.5 hours at 150°C (Test 1).

100 parts of chalk were treated in the same way with 0.5 parts of copolymer according to Example 1 (test 2) and with a mixture of 0.5 parts of propyl trimethoxysilane and 0.5 parts of copolymer according to Example 1 (test 3).

The degree of water repellancy of the chalk can be deduced from its wettability by water. Two tests were carried out.

1. With the base of a test tube, a depression was formed in a chalk sample and a drop of water 5 mm in diameter was placed in it. With the chalk which had not been made water repellent the drop was immediately absorbed; with the water repellent chalk the drop slowly evaporated into the air.
2. A small quantity of chalk was sprinkled onto water. The untreated chalk and the chalk not made water repellent sank immediately, whereas the water repellent chalk floated for at least 24 hours on the surface.

The results of these two tests are given in the following Table 6.

TABLE 6

Chalk Sample	Test 1	Test 2
Untreated chalk	immediately absorbed	sank immediately
Chalk treated with propyl trimethoxysilane	immediately absorbed	sank immediately
Chalk treated with copolymer according to Example 1	immediately absorbed	sank immediately
Chalk treated with mixture of propyl trimethoxysilane and copolymer according to Example 1	evaporated slowly into the air	remained on the surface for at least 24 hours

EXAMPLE 7

In a three necked flask equipped with a stirrer, an inlet tube for nitrogen and a reflux cooler with a calcium chloride tube, 147 g of maleic acid anhydride (1.5 mol) were dissolved, while being stirred and while nitrogen was introduced, in 510 g of vinyl triethoxysilane (2.7 mol) at 70°C. When a solution had been formed, 3.9 g of dicumyl peroxide were added and the temperature was raised to 130°C. At this temperature the reaction began. The heat evolved by polymerisation was removed by cooling. At this point, the temperature was in the range of 130 to 150°C. After the reaction had ceased, stirring was continued for a further 3 hours at 130°C, at which point the reaction had ended.

The excess vinyl triethoxysilane was first removed under a water jet vacuum at 60°C with the temperature rising to 130°C. The residual monomer was removed under an oil pump vacuum (0.1 mm Hg), and 480 g of a solid, slightly yellow tinted resin were obtained. The theoretical yield with a strictly alternating copolymer would be 432 g. The copolymer contains vinyl trialkoxy units with a number greater than 1. This is contingent on the use of an excess of vinyl triethoxysilane, which is necessary to achieve complete copolymerisation of the maleic anhydride. This is itself necessary as the residual monomer (i.e. maleic anhydride) is difficult to remove and can give rise to problems. The copolymer had a softening point of 75°C.

EXAMPLE 8

288 g of a vinyl triethoxysilane/maleic anhydride copolymer produced according to Example 7 were heated with 46.07 g of ethyl alcohol for 8 hours while being stirred. The temperature was initially maintained at 80°C until the fluid component of the ethyl alcohol

had completely reacted, i.e. until there was no longer any reflux. The reaction mixture was then heated to 100°C.

The solidification point of the product obtained was determined, and an IR spectrum was taken. The reaction of the extinctions of the CO ester group to the stretching vibration of the asymmetric CO anhydride group (E_E/E_A) was determined, this being an indication of the degree of esterification.

At 20°C, the half ester obtained was light yellow and very viscous. Its solidification point was -22.5°C. The ratio E_E/E_A was 1.10, and thus its mol percentage of anhydride groups was about 31, corresponding to 69 mol % of half ester. Its elemental analysis was as follows:

theoretical:	C:50.29%	H:7.78%	O:33.53%	Si:8.38%
found:	C:49.06%	H:7.69%	O:-	Si:8.91%

EXAMPLE 9

288 g of a vinyl triethoxysilane/maleic anhydride copolymer produced according to Example 7 were stirred with 58.8 g of allyl alcohol for 8 hours at 60°C.

At 20°C, the polymer obtained was a homogeneous, light yellow viscous melt whose solidification point was about -16°C. Its E_E/E_A ratio was 0.88, and thus its mol percentage of anhydride groups was about 36. Its elemental analysis was as follows:

theoretical:	C:52.02%	H:7.51%	O:32.37%	Si:8.09%
found:	C:50.73%	H:7.45%	O:-	Si:8.67%

EXAMPLE 10

Example 9 was repeated except that the reaction temperature was held at 100°C. At the beginning of the reaction the allyl alcohol boiled with reflux. The other reaction conditions were the same as in Example 9.

The polymer obtained had a solidification point of -45°C. Its E_E/E_A ratio was about 1.11, i.e. its proportion of anhydride groups was about 31 mol %. Its elemental analysis was as follows:

found:	C:50.67%	H:7.78%	Si:8.51%
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EXAMPLE 11

Under the reaction conditions of Example 10, 288 g of vinyl triethoxysilane/maleic anhydride copolymer (produced according to Example 7) were reacted with 242 g of cetyl alcohol.

The polymer obtained was a homogeneous, light yellow melt with a solidification point of +15.4°C. Its E_E/E_A ratio was 1.25, i.e. its mol percentage of anhydride groups was about 29. Its elemental analysis was as follows:

theoretical:	C:63.4%	H:10.19%	O:21.13%	Si:5.28%
found:	C:63.88%	H:10.54%	O:-	Si:5.67%

EXAMPLE 12

Example 11 was repeated except that the reaction mixture was additionally heated to 100°C with 0.46 g of toluenesulphonic acid for 24 hours. The solidification point of the polymer obtained was about +13°C. Its E_E/E_A ratio was 3.45, i.e. its proportion of anhydride groups was about 13 mol %.

EXAMPLE 13

In the same way as Example 11, 288 g of vinyl triethoxysilane/maleic anhydride copolymer were reacted with 130.2 g of 2-ethyl hexanol-1 at 100°C for 8 hours.

The product obtained had a solidification point of -41°C, and a proportion of anhydride groups of about 28 mol % ($E_E/E_A = 1.31$). Its elemental analysis was as follows:

theoretical:	C:57.41%	H:9.09%	O:26.79%	Si:6.70%
found:	C:56.76%	H:9.32%	O:-	Si:7.13%

EXAMPLE 14

In the same way as Example 11, 288 g of vinyl triethoxysilane/maleic anhydride copolymer were heated with 72 g of butanol at 100°C for 8 hours.

The polymer obtained had a solidification point of -14.5°C, and a proportion of anhydride groups of about 27 mol % (EE/EA = 1.38). Its elemental analysis was as follows:

theoretical:	C:53.05%	H:8.28%	O:30.93%	Si:7.73%
found:	C:51.41%	H:8.47%	O:-	Si:8.46%

EXAMPLE 15

300 g of a vinyl triethoxysilane/maleic anhydride/maleic acid half ester copolymer, produced according to Example 8, were dissolved in approximately 300 ml of ethanol. The solution obtained was dripped into 3 litres of desalted water with vigorous stirring. A fine, white deposit formed.

The deposit was easily isolated from the aqueous phase by filtering or centrifuging, and was subsequently washed. It was then dried in a circulating air drying cabinet at 50°C. A white powder was obtained in a yield of 220 g.

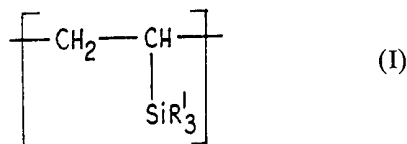
The powder obtained was a copolymer containing maleic anhydride units, maleic acid units, and vinyl silanol units (or vinyl siloxane units resulting from cross-linking). The siloxane units may be easily broken by dilute alkalis (e.g. a 1% aqueous ammonia solution) whereupon a solution is produced. The hydrolysate of the vinyl alkoxysilane/maleic acid/maleic acid half ester copolymers therefore contains in the dissolved state vinyl silanol units as well as maleic acid units. When a film is formed, or when precipitation occurs during the hydrolysis, these vinyl silanol units are partially converted to vinyl siloxane units, depending upon the pH.

EXAMPLE 16

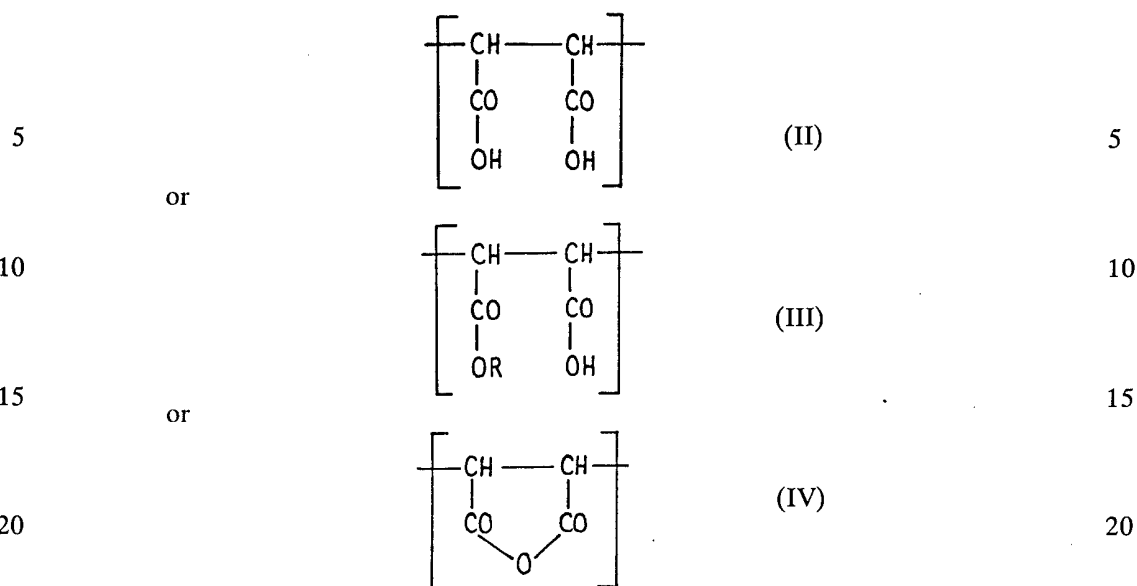
Results similar to those obtained in Examples 8 to 15 were obtained by using, instead of the vinyl alkoxysilane/maleic anhydride copolymer according to Example 7, copolymers obtained from other vinyl alkoxysilanes, namely vinyl trimethoxysilane, vinyl tributoxysilane and vinyl methyl diethoxysilane. The copolymers obtained were esterified and/or hydrolysed in the same manner.

WHAT WE CLAIM IS:

1. A solution for improving the adhesion between an organic polymer and a metallic surface, an inorganic oxidic surface (as herein defined) or an inorganic sulphidic surface and for forming a coating on a metallic surface, an inorganic oxidic surface (as herein defined), an inorganic sulphidic surface or a plastics material surface, which solution comprises water, or a mixture of water with one or more solvents miscible therewith, having dissolved therein (a) an organosilane containing at least one hydrolysable group, and (b) a copolymer comprising (i) structural units having the general formula:

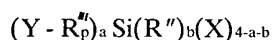


wherein R' is a radical selected from -OH and -[O]⁻, and (ii) one or more structural units having the general formulae:



wherein R is a hydrocarbyl group containing from 1 to 20 carbon atoms, the sum of the number of units of formulae (II), (III) and (IV) being not greater than the number of units of formula (I).

2. A solution as claimed in claim 1, wherein the organosilane has the general formula:



wherein a is 1 or 2, b is 0, 1 or 2 and p is 0 or 1, with the proviso that $a + b$ is not 4; R is an alkylenc group containing from 1 to 8 carbon atoms or an arylene group; R'' is an alkyl group containing from 1 to 4 carbon atoms or a phenyl group; X is a hydrolysable group; and Y is a functional group, a methyl group or a vinyl group.

3. A solution as claimed in claim 1 or 2, wherein the hydrolysable group X of the organosilane is an alkoxy group containing from 1 to 8 carbon atoms whose alkyl chain is optionally interrupted by one or more -O- linkages, or a halogen atom.

4. A solution as claimed in claim 3, wherein the organosilane is β -aminoethyl triethoxysilane, γ -aminopropyl trimethoxysilane, δ -aminobutyl trimethoxysilane, β -aminoethyl- γ -aminopropyl trimethoxysilane, α -methyl- β -aminoethyl triethoxysilane, N-dimethyl- γ -aminopropyl triethoxysilane, γ -glycidyloxypropyl trimethoxysilane, γ -glycidyloxypropyl tributoxysilane, β -3,4-epoxycyclohexylethyl trimethoxysilane, γ -mercaptopropyl trimethoxysilane, β -mercaptoethyl triethoxysilane, γ -methacryloxypropyl trimethoxysilane, isobutyl trimethoxysilane, vinyl trimethoxysilane or γ -chloropropyl trimethoxysilane.

5. A solution as claimed in any of claims 1 to 4, wherein the organosilane is present in an amount of from 0.001 to 60% by weight.

6. A solution as claimed in claim 5, wherein the organosilane is present in an amount of from 0.01 to 30% by weight.

7. A solution as claimed in any of claims 1 to 6, wherein the copolymer is present in an amount of from 0.001 to 20% by weight.

8. A solution as claimed in claim 7, wherein the copolymer is present in an amount of from 0.01 to 10% by weight.

9. A solution as claimed in any of claims 1 to 8, the solution having been obtained by the method comprising dissolving in an alcohol a copolymer obtained by reacting a vinyl trialkoxysilane with maleic acid anhydride, mixing the alcoholic solution obtained with water, separating the precipitate thus formed, dissolving the separated precipitate in an aqueous alkaline medium, and mixing the solution thus obtained with the organosilane.

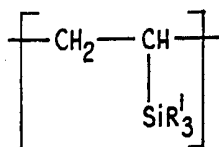
10. A solution as claimed in claim 9, the solution having been obtained by the method wherein aqueous ammonia is used as the aqueous alkaline medium.

11. A solution as claimed in claim 9 or 10, the solution having been obtained by the method wherein component (b) is used as the aqueous solution or as a solution in an organic solvent miscible with water.

12. A solution as claimed in any of claims 1 to 11, wherein R contains from 1 to 10 carbon atoms.

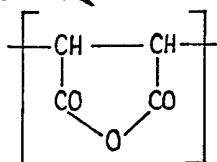
13. A solution as claimed in any of claims 1 to 12, wherein R is an alkyl group.

14. A solution as claimed in any of claims 1 to 8, wherein the copolymer comprises structural units having the general formula:



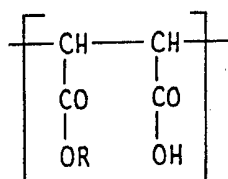
(V)

and structural units having the general formula:



(VI)

modified in that from 50 to 100% of the latter units are replaced by units having the general formula:



(VII)

wherein R and R' are as defined in claim 1, the sum of the number of units of formulae (VI) and (VII) being not greater than the number of units of formula (V).

15. A solution as claimed in claim 14, wherein the copolymer is a copolymer obtained by reacting a copolymer of a vinyl trialkoxysilane and maleic anhydride with an alcohol having the general formula ROH wherein R is as defined in claim 1, and by hydrolysing the alkoxy groups of the reaction product.

16. A solution as claimed in claim 15, the copolymer having been obtained by carrying out the reaction in the presence of a catalyst.

17. A solution as claimed in any of claims 14 to 16, wherein R is a straight-chain or branched-chain alkyl group containing from 1 to 20 carbon atoms.

18. A solution as claimed in any of claims 14 to 16, wherein R is an unsaturated hydrocarbonyl group containing from 3 to 11 carbon atoms.

19. A solution as claimed in any of claims 14 to 16, wherein R is a cycloaliphatic group containing 6, 7 or 8 carbon atoms.

20. A solution as claimed in any of claims 14 to 17, wherein R contains from 1 to 10 carbon atoms.

21. A solution as claimed in claim 1, substantially as described in any of the foregoing Examples 1 to 6.

22. A solution as claimed in any of claims 1 to 8, wherein the copolymer is a hydrolysate of a copolymer substantially as described in any of the foregoing Examples 7 to 14 and 16, or a hydrolysate substantially as described in Example 15.

23. A substrate having a metallic surface, an inorganic oxidic surface (as herein defined) or an inorganic sulphidic surface, which surface has been treated with a solution as claimed in any of claims 1 to 23 to improve the adhesion of an organic polymer subsequently adhered thereto.

24. A substrate having a metallic surface, an inorganic oxidic surface (as herein defined), an inorganic sulphidic surface or a plastics material surface, which surface has thereon a coating formed from a solution as claimed in any of claims 1 to 22.

25. An organic polymer having mixed therewith a solution as claimed in any of claims 1 to 22 to improve the adhesion of the polymer to a substrate when subsequently adhered thereto.

13. A solution as claimed in claim 12, containing carbon atoms.
 14. A solution as claimed in claim 13, containing an alkyl group.
 15. A solution as claimed in claim 14, containing a copolymer comprising

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wherein R is defined in claim 1, the sum of the number of units of formula (V) and (VI) being not greater than the number of units of formula (V).

wherein R and R' are as defined in claim 1, the sum of the number of units of formula (V) and (VI) being not greater than the number of units of formula (V).

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