



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/US97/22657 <b>(22) International Filing Date:</b> 11 December 1997 (11.12.97) <b>(30) Priority Data:</b> 767,458 16 December 1996 (16.12.96) US <b>(71) Applicant:</b> VERNAY LABORATORIES, INC. [US/US]; 120 E. South College Street, P.O. Box 310, Yellow Springs, OH 45387-0310 (US). <b>(72) Inventors:</b> ROSEBOOM, Frederick; Kretalaan 47, NL-7577 KK Oldenzaal (NL). VAN DER AAR, Cornelius, P., J.; Alexanderstraat 56, NL-7553 WZ Hengelo (NL). BANT- JES, Adriaan; Langenkampweg 95, NL-7522 LL Enschede (NL). FENG, Minhua; Unit 1, 39 Milson Street, South Perth, W.A. 6151 (AU). <b>(74) Agents:</b> PEACOCK, Bruce, E. et al.; Biebel & French, 2500 Kettering Tower, Dayton, OH 45423 (US).	<b>(81) Designated States:</b> CN, JP, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i>	
<b>(54) Title:</b> POLYMERIC COUPLING AGENTS FOR THE ADHESION OF MACROMOLECULAR MATERIALS AND METAL SUBSTRATES		
<b>(57) Abstract</b> <p>Polymeric coupling agents incorporate within their structures co-vulcanizable groups such as alkenyl, epoxide, acrylate and/or acrylamide, and metal-complexing groups such as carboxylic, oxime, amine, hydroxamic and/or iminodiacetic groups. The polymeric coupling agents are useful in the adhesion of certain substrates and are particularly useful as adhesives for the adhesion of rubbers with metals. Syntheses of the novel polymeric coupling agents are provided.</p>		

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POLYMERIC COUPLING AGENTS FOR THE ADHESION  
OF MACROMOLECULAR MATERIALS AND METAL SUBSTRATES

Field Of The Invention

This invention relates generally to novel  
5 adhesives, and more specifically relates to polymeric  
coupling agents acting as adhesives which incorporate  
within their structures polymer backbones, and, bonded to  
the backbone as pendant groups, co-vulcanizable groups  
and chelating groups. The invention also relates to  
10 methods of synthesizing and using such polymeric coupling  
agents as adhesives.

Background Of The Invention

The adhesives nowadays used for rubber to metal  
bonding are either based on silane coupling agents (see  
15 "Silane Coupling agents", F.P. Plueddemann, Plenum Press,  
New York, 1990) or a mixture of resins, elastomers and  
fillers which suspended or dissolved in organic solvents  
(see "Rubber to metal bonding", P.M. Lewis in Handbook of  
Adhesion, D.E. Packham(ed.), Longman Scientific &  
20 Technical, Harlow, 1992). A specific kind of adhesion  
promoter is a galvanic layer of brass, mainly used in  
tire cord applications (see W.J. van Ooij, Rubber Chem.  
Technol., 52, 4.37 (1979)). Most of the adhesives are  
applied in a two layer system which contains an adhesive  
25 layer and a primer layer to obtain durable joints with  
high chemical resistance, thermal stability and  
hydrolytical stability. There are still some problems to  
achieve the required properties in specific rubber to  
metal adhesion with the adhesives.

30 Coupling agents are defined as materials that

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improve adhesion by forming primary bonds to the substrates, applied coatings, or composite materials. The silane coupling agents usually incorporate three hydrolyzable groups and another reactive group on silicon. The hydrolyzable groups are essential when applied to inorganic substrates, whereas the other reactive group is able to react with organic substrates. The main applications of silane coupling agents are in the technology of composites, the paint industry, and in the case of rubber to metal bonding such as the bonding of fluororubbers to metal substrates. It is noted that various organofunctional silanes and a few non-silane coupling agents such as methylacrylate-chrome complex (Volan A ) have shown promise as true coupling agents. However, some cases such as the adhesion of EPDM rubber with stainless steel have not been investigated with the silane coupling agents.

Accordingly, it is an object of the present invention to provide novel polymeric coupling agents which will be used as adhesives for the adhesion of some dissimilar substrates such as rubbers with metals.

It is another object of the invention to provide polymeric coupling agents which can be applied in preferred solvents such as water and ethanol.

It is still another object of the invention to provide polymeric coupling agents which incorporate within their structures metal-complexing groups as well as co-vulcanizable groups.

It is a further object of the invention to provide methods of synthesizing the novel polymeric coupling agents.

It is still a further object of the invention

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to provide methods of using the novel polymeric coupling agents for the adhesion of macromolecular materials with metal substrates, and particularly for the adhesion of rubbers with metals.

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SUMMARY OF THE INVENTION

The above and other objects are met by the provision of a coupling agent that is water or alkanol-soluble or dispersible and which provides adhesive efficacy in a wide variety of applications such as rubber with metals. For this reason, water or ethanol-soluble polymers with co-vulcanizable groups are designed. These co-vulcanizable groups can react with the vulcanizable sites of the macromolecular elastomeric materials during vulcanization to form covalent bonds. In addition, the polymeric coupling agents having metal-complexing groups are particularly desirable in contrast to the hydrolyzable groups in silane coupling agents. Through the chelating groups, coordination bonds may be formed between the polymeric coupling agents and the surfaces of metals.

Specific polymer chains are chosen to make the polymers water or ethanol-soluble or dispersible. In this regard, polyacrylic acid, polyacrylamide, and polyvinylamine polymers comply with this requirement and are commercially available in either the polymeric form or in the corresponding monomers. In the case of polyacrylic acid, the COOH functionality thereof provides the desired metal-complexing or chelating function.

The  $\begin{array}{c} \text{O} \\ || \\ -\text{C} \end{array}$ -NH<sub>2</sub> (amido) and the -NH<sub>2</sub> (amino) functionality of respectively the polyacrylamide and polyamine polymers similarly provides chelation sites along the polymer backbone.

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The availability and reactivity of these unsaturated monomers and their corresponding polymers (i.e., polyacrylic acid, polyacrylamide, and polyamine) make them convenient starting materials onto which co-vulcanizable groups or additional chelate functionality may be provided by reaction of compounds containing such co-vulcanizable or chelate groups with the above polymers.

Other exemplary chelating groups that may be mentioned as useful for bonding to the backbone chain include hydroxamic acid  $\begin{array}{c} \text{-C} \text{ -NOH} \\ \parallel \quad | \\ \text{O} \quad \text{H} \end{array}$ , and iminodiacetic acid groups



and others.

Co-vulcanizable groups that may be attached to the polymer backbone include functionalities having an unsaturated bond (i.e. vulcanizable olefinic bond) at a terminal carbon atom. Exemplary members of this group include alkenyl ( $\text{C}_1\text{-C}_6$ ) substituted or unsubstituted alkyl ( $\text{C}_1\text{-C}_6$ ) ethers, N-substituted acrylamido groups and others. These functional groups, upon vulcanization, via heat or other means, provide for the formation of strong, covalent bonds with the olefinic elastomer or rubber bonds.

#### Detailed Description Of The Invention

The present invention first of all provides novel polymeric coupling agents which can be used as adhesives for the adhesion of dissimilar substrates and especially for the adhesion of rubbers with metals.

The inventors have demonstrated the

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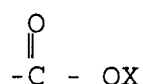
effectiveness of novel polymeric coupling agents having chelating groups and co-vulcanizable groups within their structures. The chelating properties of the polymeric coupling agents in combination with their bonding ability  
5 make them effective coupling agents in adhesion of some dissimilar substrates. The new polymeric coupling agents display a high affinity for iron as well as other metals, and are thus effective for adhesion of metals.

The water or ethanol-soluble adhesives comprise  
10 a polymeric backbone constituent that may, for example, be formed via conventional free radical chain addition polymerization of vinyl monomers, step reaction (condensation) polymerization or ionic and/or coordination chain (addition) polymerization techniques.

15 Exemplary organic synthetic polymers include polyamines, polyamides, polyacrylamides, polyethers, polyacrylic acid, polyacrylate, polyethylenes, polyesters and polyurethanes.

Generally, the chelating groups attached to the  
20 polymeric backbone may, for example, be provided by the groups selected from the class consisting of

(a) Carboxylic groups of formula



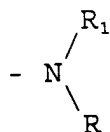
25 X = Na, H, or K

(b) Oxime groups of formula



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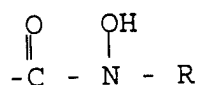
(c) Amine groups of formula



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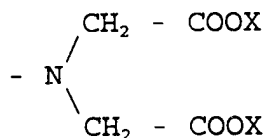
 $\text{R}_1 = \text{R}_2 = \text{H}, \text{CH}_3 \text{ or } \text{CH}_2\text{CH}_3$ 

(d) Hydroxamic acid groups of formula

 $\text{R} = \text{H}, \text{CH}_3 \text{ or } \text{CH}_2\text{CH}_3$ 

10

(e) Iminodiacetic acid groups of formula

 $\text{X} = \text{H}, \text{Na} \text{ or } \text{K}; \text{ and}$ 

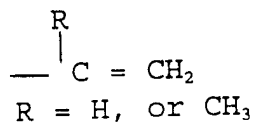
15

(f) Mixtures of two or more of the above groups

Generally the co-vulcanizable groups that are attached to the polymer backbone as pendant polymer groups may, for example, be provided by the groups selected from the class consisting of

20

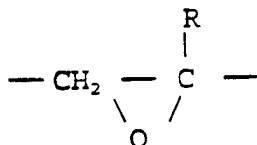
(a) Alkenyl groups of formula





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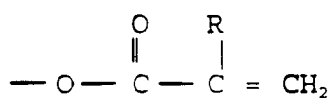
(b) Epoxide groups of formula



5

R = H, CH<sub>3</sub> or CH<sub>2</sub>CH<sub>3</sub>

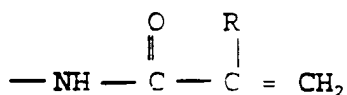
(c) Acrylate groups of formula

R = H, or CH<sub>3</sub>

10

(d) Amino groups -NH<sub>2</sub>

(e) Acrylamide groups of formul

R = H, or CH<sub>3</sub>; and

15

(f) Mixtures of two or more of the above groups

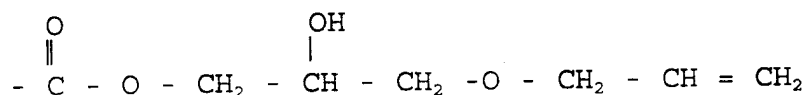
It is possible to introduce spacers between the chelating or (co)vulcanizable groups with the polymer backbone. Thus a polymeric coupling agents suitable for the process of the present invention may be represented generally by the formula

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wherein R is a co-vulcanizable group with or without a suitable space. M is a metal-complexing group with or without a suitable spacer. For example, the polymer chain may be polyacrylic acid, M may be a carboxylic group and R may be a group such as



In accordance with the present invention, a process for the preparation of polymeric coupling agents as defined above can be characterized in that chelating groups and co-vulcanizable groups are covalently fixed to the polymer backbone. Any suitable means of covalently fixing chelating groups and co-vulcanizable groups to the polymer backbone can be used provided that the polymeric coupling agents obtained have the necessary adhesive properties.

The chelating groups and co-vulcanizable groups as indicated above can be present in the starting polymers or introduced by modification of existing polymers and/or by the co-polymerization of suitable monomers.

As an example of an introduction of groups at a polymer backbone a polymeric coupling agent comprising carboxylic groups and a co-vulcanizable group can be prepared by copolymerization of acrylic acid with an alkenyl glycidyl ether such as allyl glycidyl



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Preparation polyacrylic Acid Derivatives

When a polyacrylic acid backbone polymer is to be used, a commercially available polyacrylic acid can be used as the precursor. The precursor can then be reacted  
5 with a compound or compounds providing additional chelation sites or vulcanizable functions in either an aqueous solution or a H<sub>2</sub>O/EtOH mixture.

For example, a commercially available polyacrylic acid from Aldrich may be reacted with  
10 hydroxylamine so as to provide -NHOH hydroxyamino functionality along the polymer backbone. The reaction may proceed as follows:

Synthesis 1 - Modification of Poly(acrylic acid) with hydroxylamine

15 (PHA): 5.0 g. poly(acrylic acid) (Aldrich) is dissolved in 40 ml water. 48.5 g Hydroxylamine-HCL (Aldrich) is mixed (500 mol%) with the reaction solution and the pH of the solution is adjusted with aqueous sodiumhydroxide to 3.5. The reaction mixture is then stirred at a temperature of  
20 100°C for 6h. The resulting yellow solution is purified by using a dialysis tube (M<sub>w</sub>=1200 g/mol) for 30h to separate the low molecular weight material. Water is dried off by freeze drying.

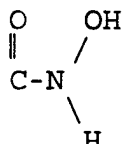
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Polyacrylic acid can be similarly modified with allylglycidylether (AGE) to provide vulcanizable pendant functionality on the polymer chain as follows:

5 Synthesis 2 - Modification of Poly(acrylic acid)  
with allylglycidylether

(PAGE): 4--10.0g of Poly(acrylic acid) (Aldrich) is dissolved in 40 ml water and 40 ml ethanol. 16.6 ml allylglycidylether (Aldrich) is mixed into the solution (100 mol%). The pH is maintained at 4.75. The reaction  
10 mixture is then allowed to stir for 5h at a temperature of 60°C. The ethanol and partly the water is evaporated. The solution is washed with chloroform or toluene, the chloroform or toluene is evaporated and the water is dried off by freeze drying.

15 If desired both hydroxamic acid groups

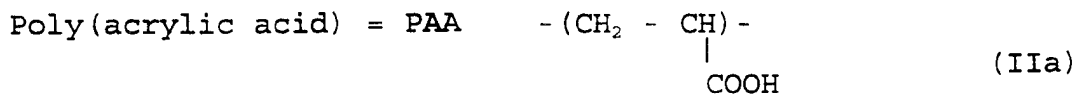


(containing                      functionality) for chelation and terminal olefinic functionality (from reaction with AGE) to provide vulcanizable sites may be incorporated along the backbone chain. This reaction may proceed in  
20 accordance with the following:

Synthesis 3

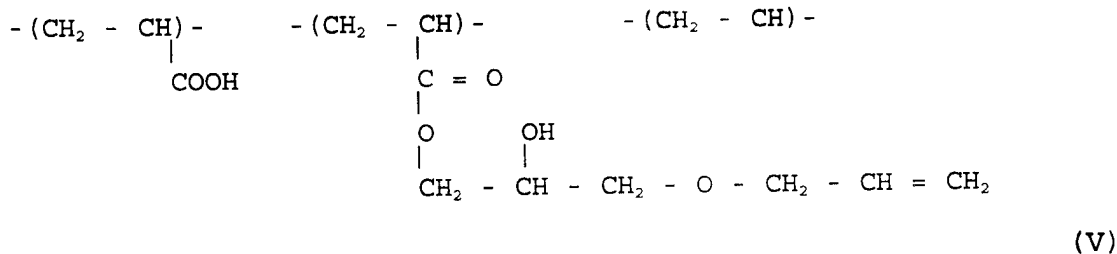
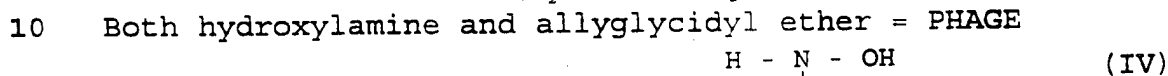
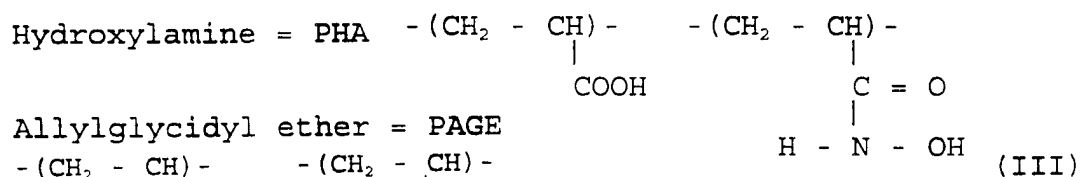
Synthesis (PHAGE): 10.0 g of the product of synthesis 1 is dissolved in 40 ml water and 40 ml ethanol. 16.6 ml allylglycidylether (Aldrich) is mixed into the reaction  
25 solution (100 mol%). The pH is 4.75. The reaction mixture is stirred for 5h at a temperature of 60°C. The ethanol and partly the water are evaporated. The solution is washed with toluene and dialyzed for 8h. The water is dried off by freeze drying to obtain a white  
30 solid.

Polymer adhesives formed via synthetic routes 1-3 have the following structural formula:



5

Modified with:



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Preparation of Polyacrylamide derivatives

Polyacrylamide is commercially available and contains  $\text{-NH}_2$  groups bonded to the acrylamido carbonyl group. These  $\text{-C} \begin{array}{c} \text{O} \\ \parallel \end{array} \text{-NH}_2$  groups provide a chelation site to chelate metal atoms or ions. Desirably, pendent vulcanizable sites may be added along the polyacrylamide chain by the following reaction.

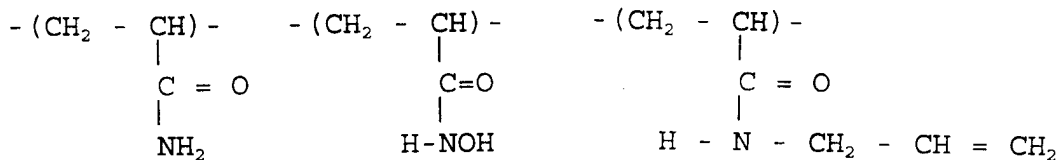
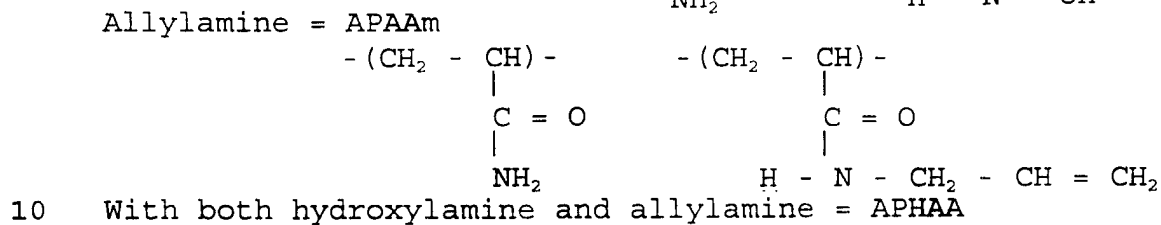
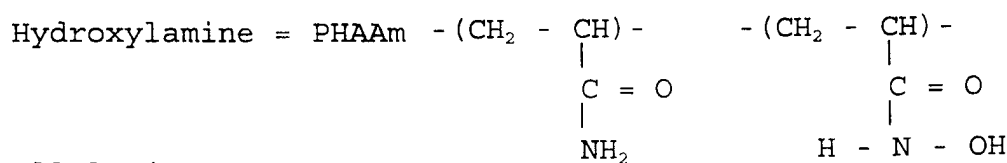
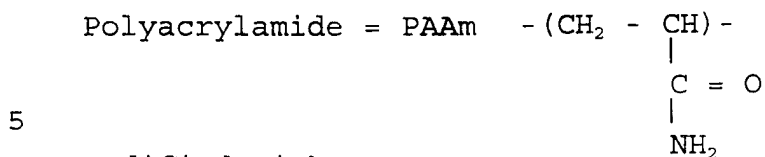
Synthesis Route 4 - Modification of Polyacrylamide with Hydroxylamine (PHAAM)

20g Polyacrylamide (Aldrich) is dissolved in 300 ml water. 100 ml 3.3 M solution of hydroxylamine ( $\text{NH}_2\text{OH} \cdot \text{HCl}$  (Aldrich)) is added. The mixture is allowed to stir at room temperature for 30 min. Then the pH of the mixture is adjusted to 12-13 with an aqueous solution of 3.9 M NaOH. The reaction is continued for 24 h at room temperature. After this reaction time, the solution is acidified to pH 1 with 3N HCl and the polymer is isolated by precipitation in methanol.

Synthesis Route 5 - Modification of polymer from synthesis route 4 (APHAAM)

20 g. of the polymer product of synthesis route 4 is dissolved in 300 ml water. 12.2 ml allylamine (Aldrich) is added. The mixture is allowed to stir for 30 min. at room temperature. The pH of the solution is adjusted to 12-13 with a 3.9 M aqueous solution of sodium hydroxide and the reaction is continued for 24 h at room temperature. After this reaction time the solution is acidified to pH 1 with 3N HCl and the polymer is isolated by precipitation in acetone.

Polymer adhesives formed via synthetic routes 4-5 have the following structural formulae:





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Preparation Polyvinylamine Derivatives

Polyvinylamine polymers are available, for example from Aldrich with Mw of about 50,000. The NH<sub>2</sub> functionality pendant from the C-C chain provides  
5 excellent chelation sites for chelating metal atoms or ions. These polymers may be modified, for example, by reaction with AGE to provide a terminal double bond for subsequent vulcanization. Also, the polyvinylamine polymers may be reacted with chloroacetic acid or  
10 chloroacetic anhydride to result in the addition of iminodiacetic acid functionality to provide chelation sites along the polymer chain.

Synthesis Route 6 - Modification of polyamine with chloroacetic acid (PALMINO).

15 25 g polyvinylamine (Aldrich) is dissolved in 100 ml water. 8.6 g chloroacetic acid (150 mol%) (Aldrich) is added and the pH is adjusted above 12. The reaction is continued for 24 h at 50°C. After this reaction time, the solution is dialyzed for 8 h with a dialysis tube (Mw  
20 = 1200g/mol) to separate the low molecular weight material. Water is dried off by freeze drying.

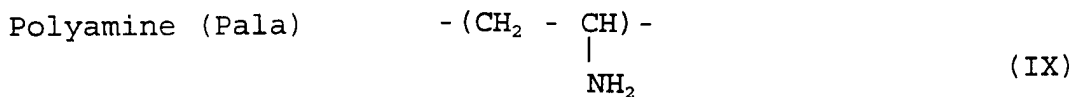
Synthesis Route 7 - Modification of polyamine with allyglycidylether (PALAGE)

25 5 g polyamine (Aldrich) is dissolved in 30 ml ethanol and 70 ml water. 13.8 ml allyglycidylether (100 mol%) is added. This reaction mixture is stirred for 24 h at 60°C. The ethanol and partly the water is evaporated. The solution is washed with chloroform and the yellow solution is dialyzed for 8 h with a dialysis tube (MW =  
30 1200g/mol) to separate the low molecular weight material. The water is dried off by freeze drying to obtain a yellow solid.

Synthesis Route 8 - Modification of Polymer of Synthesis Route 6 with allylglycidylether (PALMINOGE)

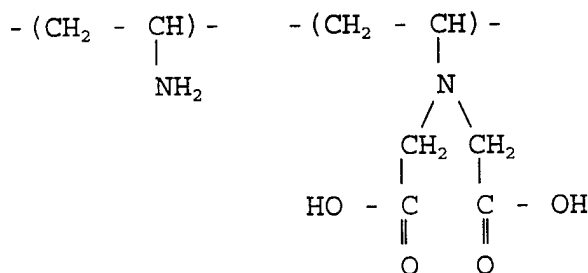
2.3 g. of the polymer obtained via synthesis route 6 is dissolved in 30 ml ethanol and 30 ml water. 7 ml allylglycidylether (100 mol%) (Aldrich) is added. The reaction mixture is allowed to stir for 24 h at 60°C. The ethanol and partly the water are evaporated. The solution is washed with toluene and the yellow solution is dialyzed for 8 h with a dialysis tube (MW = 1200 g/mol) to separate the low molecular weight material. The water is dried off by freeze drying to obtain a yellow solid.

Polymer adhesives formed via reaction of synthetic routes 6-8 have the following structural formulae:

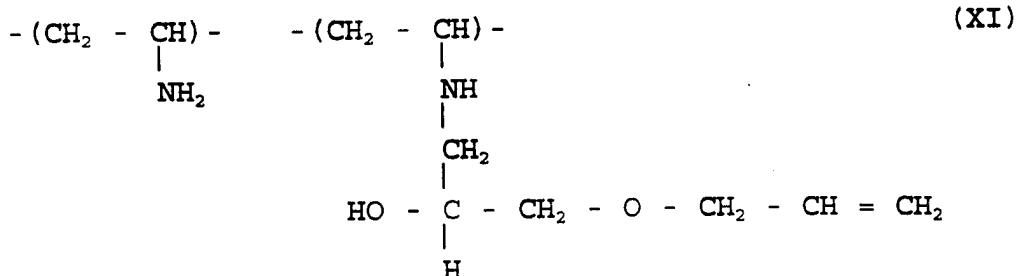


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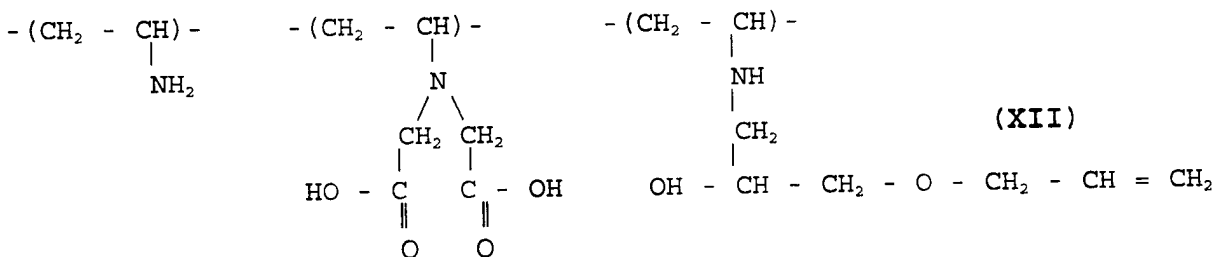
20 Chloroacetic acid = Palmino



Allyglycidylether = Palage



Modified with both chloroacetic acid and allyglycidylether = Palminoge



The invention will now be further explained with reference to a number of specific examples which are to be regarded solely as illustrative, and not as restricting the scope of the invention.

EXAMPLES

Example 1 - Polymers Prepared

Comparative polymers and polymers in accordance with the invention were prepared and tested for adhesive efficacy.

Poly(acrylic acid)s and the derivatives - Table 1

indicates the polyacrylic acid (comparative) and polyacrylic acid derivatives (copolymers in accordance with the invention that were prepared in accordance with the procedures described above.

Table 1 - Comparative Poly(acrylic acid) and  
Poly(acrylic acid) Derivatives of the Invention

Candidate No.	Polymer	MW	%HA	%AGE	
5	C-1	PAA	2000	---	---
	C-2	PAA	90,000	---	---
	C-3	PAA	250,000	---	---
	C-4	PAA	450,000	---	---
	1	PHA	2000	10-20	---
10	2	PHA	90,000	10-20	---
	3	PHA	250,000	10-20	---
	4	PHA	450,000	10-20	---
	5	PAGE	2,000	---	10-20
	6	PAGE	90,000	---	10-20
15	7	PAGE	250,000	---	10-20
	8	PAGE	450,000	---	10-20
	9	PHAGE	2,000	10-20	10-20
	10	PHAGE	90,000	10-20	10-20
	11	PHAGE	250,000	10-20	10-20
20	12	PHAGE	450,000	10-20	10-20

C = comparative

PAA = polyacrylic acid

PHA = polyacrylic acid - hydroxylamine reaction product

25 PAGE = polyacrylic acid - allylglycidylether modified product

PHAGE = polyacrylic acid - hydroxylamine - allyl glycidyl ether reaction product

HA = hydroxylamine

AGE = allylglycidyl ether

30 MW = MW of precursor polyacrylic acid

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Polyacrylamide Derivatives - Table 2 indicates the various polyacrylamide derivatives that were prepared in accordance with the procedures referred to above.

Table 2 - Polyacrylamide Derivatives

Example No.	Polymer	MW	%HA	%AA
C-5	PAAM	200,000	---	---
C-6	PAAM	5-6 x 10 <sup>6</sup>	---	---
13	PHAAM	5-6 x 10 <sup>6</sup>	reacted with A	---
14	APHAAM	5-6 x 10 <sup>6</sup>	A	13
15	PHAAM	200,000	5-10	---
16	APHAAM	200,000	5-10	C

PAAM = polyacrylamide

PHAAM = polyacrylamide/hydroxyl amine reaction product

APHAAM = polyacrylamide/hydroxylamine/allyl amine reaction product

AA = allyl amine

MW' = molecular weight of the polyacrylamide precursor

A = reacted with 120 mol% hydroxylamine \* Hcl

(Based upon 100 mol% PAAM)

B = reacted with 230 mol% allylamine

(Based upon 100 mol% PAAM)

C = reacted with 50 mol% (Based upon 100 mol% PAAM)

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Polyamine Derivatives - Table 3 indicates the various polyamine derivatives that were prepared in accordance with the synthetic procedures described above.

Table 3

Example No.	Polymer	MW	CA	AGE
C-7	PALA	50,000- 60,000	---	---
17	PALMINO	50,000- 60,000	A	---
18	PALAGE	50,000- 60,000	---	B
19	PALMINOGE	50,000- 60,000	A	B

CA = chloroacetic acid

Pala = polyamine (polyvinylamine)

Palmino = polyamine/chloroacetic acid reaction product

Palage = polyamine/allyl glycidyl ether reaction product

Palminoge = polyamine/allyl glycidyl ether/chloroacetic acid reaction product

MW' = molecular weight of the polyvinylamine precursor

A = reacted with 150 mol% chloroacetic acid

(Based upon 100 mol% Pala)

B = reacted with 100 mol% allylglycidylether

(Based upon 100 mol% Pala)

### Example 2 - Adhesion Tests

#### Procedure

In order to ascertain the efficacy of the polymeric coupling agents in providing adhesion between metal and rubber surfaces, a series of test were performed with test specimens as set forth in ISO procedures 5600 and 814.

In accordance with the ISO 5600 procedure, the test piece is composed of two conical ends of a rigid material (plastic or metal), joined by a cylinder of

- 21 -

rubber. The rigid material comprises a pair of metal  
insert parts: each containing a conical end and an  
opposed cylindrical end. The diameter of the cylindrical  
ends is 25 mm, while the half angle of the conical vertex  
5 is 45°. The two conical ends of the inserts are spaced  
apart from each other with the cylindrical rubber  
material provided, at its opposed longitudinal ends, with  
"V" shaped concavities; each adapted to mate with a  
conical end of one of the rigid inserts. The insert-  
10 rubber-insert combination is aligned so that a space of  
about 6 mm separates the tip end of one conical insert  
from the tip end of the other.

The test adhesives are applied along the  
interfacial surfaces of each of the "V" shaped  
15 concavities of the rubber material and the conical ends  
of the inserts. The so formed test pieces are vulcanized  
in a suitable transfer mould for 6 minutes at 185°C under  
a clamp pressure of 60 bar. The test pieces were then  
allowed to relax for 16 h at 21°C. In some cases, (where  
20 indicated) the test pieces were then placed in an  
autoclave in a 50/50 solution of monoethylene glycol and  
water for 4 or 22 hours at 135°C.

After the preparation, the test pieces are  
placed in the fixtures of a tensile testing machine. The  
25 maximum force used to break the adhesion and/or the  
rubber fraction was recorded.

Under the testing procedure set forth in ISO-  
814, a rubber disk and two circular metal plates are  
provided. The surface of each of the plates is coated  
30 with the candidate adhesive material with the rubber  
cylinder then interposed between the two coated metal

- 22 -

plate surfaces. The assembly is then heated under suitable pressure to vulcanize the rubber. After curing, the tensile strength needed to break the adhesion is measured.

5 All of the metal parts are either cleaned by degreasing with trichloroethylene or with a water based degreasing system. The polymeric coupling agents are typically applied in 1% solution to the metal surface. The parts are then dried for 20 min. at 120°C and are  
10 then ready for molding.

Tested metal alloy surfaces are as follows:

Stainless Steel	X12CrMoS17
Mild Steel	9SMn36
Brass	CuZn39Pb3
15 Aluminum	AlSiMg

### Example 3 - Adhesion Tests

#### Polyacrylic Acid and Derivatives

Results of ISO 5600 and 814 procedure adhesive tests on acrylic acid and acrylic acid derivatives are  
20 shown in Tables 4 and 5. Experimental conditions for these tests were in accordance with the procedures specified above, except where noted to the contrary.



Table 4

TABLE 4									
		Adhesion							
		ISO-5600				ISO-814			
Product Code	Mw	BA[N]	%R	AA[N]	%R	BA[N]	%R	AA[N]	%R
Poly (acrylic acid)									
PAA	2000	106.7	0	55.1	0	97.6	0	fdm	
PAGE	2000	564.0	100	300.2	0	530.5	80	272.8	10
PHA	2000	134.0	0	182.9	0	63.1	0	90.4	0
PHAGE	2000	577.3	100	576.8	100	434.4	0	416.2	10
PAA	450000	568.0	100	547.8	100	622.4	50	568.2	40
PHA	450000	354.1	0	237.1	0	436.9	10	366.7	10
PHAGE	450000	381.5	0	333.9	0	423.2	0	395.0	0

15 BA[N] = force in Newtons needed to separate the test pieces before the test pieces had been subjected to autoclaving

20 %R = % a test piece separates due to failure of the EPDM cylinder.

25 AA[N] = force needed in Newtons to separate the test pieces after the test pieces had been subjected to autoclaving procedure as set forth above. The candidate adhesives were applied to the test surfaces via dip application of 1% aqueous solutions.

fdm - failure during molding

30 MW = molecular weight of the polyacrylic acid precursor

rubber = EPDM

metal = stainless steel

Table 5

TABLE 5 ISO-5600							
PCA	Can#	BA[N] (1)		%R	AA[N] (1)		%R
PAA-2000	C1	80.3	(7.8)	0	77.9	(2.9)	0
PAA-90000	C2	551.3	(5.4)	75	531.4	(6.2)	75
PAA-250000	C3	492.7	(33.1)	5.80	508.7	(16.6)	75
PAA-450000	C4	571.3	(12.9)	100	522.3	(27.7)	100
PHA-2000	1	27.7	(17.3)	0	fda		0
PHA-90000	2	554.6	(10.6)	75	529.2	(6.8)	75
PHA-250000	3	556.9	(0.8)	70	505.4	(20.6)	75
PHA-450000	4	556.3	(7.0)	85	509.1	(23.8)	75-95
PAGE-2000	5	574.0	(8.2)	100	559.1	(4.4)	100
PAGE-90000	6	334.4	(55.6)	40	372.0	(34.6)	30-50
PAGE-250000	7	575.2	(3.4)	100	553.0	(4.7)	80-100
PAGE-450000	8	482.7	(67.4)	35-100	311.7	(90.3)	40-50
PHAGE-2000	9	474.4	(78.3)	25-55	530.3	(19.5)	60-95
PHAGE-90000	10	579.6	(4.9)	100	564.6	(7.2)	100
PHAGE-250000	11	568-0	(9.5)	100	562.4	(5.5)	100
PHAGE-450000	12	327.2	(74.0)	15-25	396.4	(120.8)	5-50

fda = failure during autoclave

Can = candidate

PCA = polymeric coupling agent

Example 4

In order to contrast the efficacy of the candidate adhesives in accordance with the invention to several commercially available silane based adhesives, ISO 5600 tests were undertaken with the results thereof shown in Table 6.

Table 6

TABLE 6						
Silane	BA[N] (1)		%R	AA[N] (1)		%R
10 Chemosil 511 (10% dip)	580.2	(18.0)	100			
Megum 3290 (10% dip)	258.5	(57.5)	10			
15 Megum 3290 (20% dip)	327.2	(15.0)	15			
Megum 3290-1 (20% dip)	344.4	(88.9)	5	341.4		5
Megum 3290-1 (10% dip)	575.2	(6.1)	100			
20 Megum 3290-1 (10% spray)	603.9	(15.7)	100	546.3	(37.6)	100
Megum 3270/ Megum 14550	575.4		100			

25 (% dip) indicates that the % concentration of the adhesive in ethanol (denatured) that was used for dip application of the adhesive onto the requisite test surfaces.

Chemosil 511 = silane mixture; available Henkel

30 Megum 3290 = silane mixture; available Chemetall

Megum 3290-1 = silane mixture; available Chemetall

Megum 3270/Megum 14550 = unidentified mixtures of reactive polymers and pigments dissolved in MEK and/or xylene; available Chemetall

35

(1) = standard deviation

Example 5

A Series of tests were run utilizing the above ISO-5600 procedure but applying the adhesive to the test surfaces by spraying. In these tests, the coupling agents were sprayed onto preheated (120°C) metal inserts. Layer thicknesses were controlled by maintaining an approximately constant spraying time per piece sprayed. Results of this test are shown in Table 7.

10 Table 7 - Polymeric Coupling Agents Applied By Spraying

TABLE 7					
PCA	Can #	BA <sup>1</sup> [N]	%R	AA[N]	%R
PAA-2000	C-1	106.7	0	55.1	0
PAGE-2000	4	564.0	100	300.2	0
15 PHA-2000	1	134.0	0	182.9	0
PHAGE-2000	9	577.3	100	576.8	100
PAA-450000	C-4	568.0	100	547.8	100
PHA-450000	4	354.1	0	237.1	0
20 PHAGE-450000	12	381.5	0	333.9	0

BA = Before autoclave

AA = After autoclave (4h, 135°C, 50/50 glycol/water);  
results in minimum Tensile strength [N] and Rubber  
Retention [%R]

25 Rubber - EPDM; Metal = stainless steel alloy

Example 6

Other adhesive efficacy tests were conducted using the ISO 5600 procedures modified as stated. Results are shown in Table 8.

5

Table 8

TABLE 8							
PCA	Can#	BA[N] (1)		%R	AA[N] (1)		%R
PHAGE-250000(.1% dip)	11	383.0	(19.3)	50	225.8	(31.9)	10
PHAGE-250000(.5% dip)	11	545.2	(5.7)	90	525.9	(15.4)	100
PHAGE-250000(1% dip)	11	584.5	(8.2)	100	523.1	(6.8)	100
PHAGE-250000(2% dip)	11	585.7	(6.7)	100	521.4	(7.6)	100

10

BA = Before autoclave;

15 AA = After autoclave (12h, 135°C, 50/50 glycol/water);  
results in maximum Tensile strength [N] and Rubber  
Retention [%R]

(1) standard deviation

Example 7

Commercial adhesives have their own curing systems. When a polymeric coupling agent is applied on the metal surface, it is ready to react with rubber. It does not need any curing time. Thus, it is expected that there is a dependency for the commercial adhesives on temperature and there is no dependency on temperature for the polymeric coupling agents, as long as the rubber is not scorched.

	PCA-11 PHAGE-250000		Commercial adhesive Megum 3200-1 (10%)		Commercial adhesive Megum 3270/Megum 14550	
T[°C]	BA[N]	%R	BA[N]	%R	BA[N]	%R
180	543	100	579	100	565	100
190	556	100	-	-	582	100
200	566	100	544	70	478	50
210	579	100	424	0	45	0

T = Vulcanization temperature [°C]

BA = Maximum Lensile Strength before autoclave [N]

Rubber-EPDM; Metal-Stainless steel

- = not executed

Example 8

The previous examples all showed adhesion between EPDM-rubber and Stainless Steel. In this example, the adhesion between EPDM-rubber and other metals were tested with the polymeric coupling agents.

5

10

15

	C4 PAA-450000		C1 PAA-2000 (1.0%)		PCA-11 PHAGE-250000 (1.0%)		PCA 7 PAGE - 250000 (1.0%)	
[BA]								
Metal-Type	[N]	%R	[N]	%R	[N]	%R	[N]	%R
Mild Steel	526.4	100	57.6	0	542.2	100	534.8	100
Aluminium	514.6	100	21	0	527.8	100	535.8	100
Brass	288.1	20	11.6	0	75.8	0	201	5
(AA)								
Metal-Type								
Mild Steel	485.3	100			486.3	100	489.9	100
Aluminium	480.4	100			474.4	100	491.3	100
Brass	78.8	0			19.4	0	39	0

Example 9

Adhesive efficacy tests were performed with some of the polyacrylamide and polyamine based polymeric coupling agents. Results are shown in Table 9. Rubber here is EPDM and the metal surfaces are stainless steel.

Table 9

TABLE 9								
PCA	Can#	BA[N] (1)		%R	AA[N] (1)		%R	
10 PAAm200000	C-5	286.1	(0.83)	40	186.0	(82.3)	5-20	
PAAm5-6E6	C-6	234.1	(25.9)	0-15	58.1		0	
PHAAm200000	15	290.0	(74.3)	5-30	216.4	(67.2)	0-20	
PHAAm5-6E6	13	126.1	(35.5)	0	77.5	(0.8)	0	
APHAAm200000	16	120.7	(33.8)	0	34.3	(22.0)	0	
15 APHAAM5-6E6	14	fdm		0	fdm		0	
PALA50-60000	C-7	227.0	(12.3)	5.15				

BA = Before autoclave;

20 AA = After autoclave (4h, 135°C, 50/50 glycol/water);  
Results in maximum Tensile strength [N] and Rubber Retention [%R]

(1) = standard deviation

fdm = failure during molding



Example 10

Adhesive efficacy tests were performed with some of the polyamine based polymeric coupling agents for EPDM-rubber to stainless steel.

5	PCA	BA [N]	%R	AA [N]	%R
	Polyamine (1%) - C7	408	60	132.9	0
	Palmino (1%) - 17	285.0	0	142.6	0
	Palminoge (0.5%) - 19	537.4	100	476.4	100
	Palage (0.5) - 18	296.7	20	220.1	0

10 Polyamine should be modified with both R and M-groups to obtain good adhesion.

Example 11

Two Polymeric Coupling Agents and Poly(acrylic acid)-C<sub>4</sub> were tested on adhesion of a variation of elastomers to stainless steel.

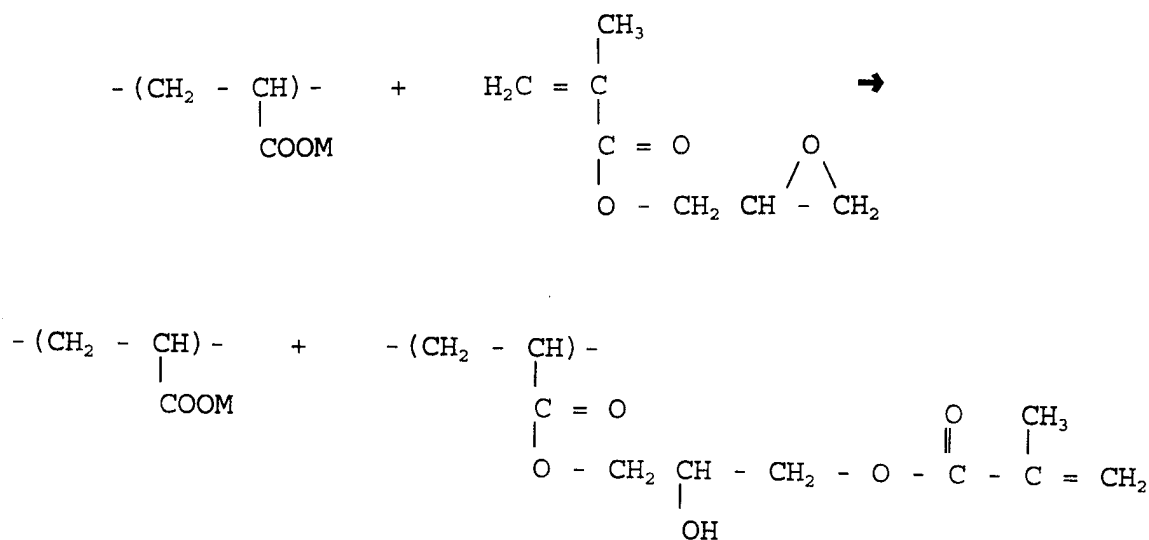
	C4 PAA-150000		PCA -11 PHAGE-250000		PCA - 19 PALMINOGE-50000	
Rubber-Type	BA [N]	% R	BA [N]	% R	BA [N]	%R
HNBR	79.2	0	485.7	0	403.9	0
FPM	102.4	0	170.5	0	567.2	100
VMQ	117.9	0	140.1	0	134.6	0
FVMQ	68.1	0	59.5	0	19.4	0
Blend Q	76.1	0	166	0	78.7	0

- HNBR = Hydrogenated Nitrile Butadiene Rubber
- FPM = Fluorocarbonrubber
- VMQ = Vinyl Methyl Silicone Rubber
- FVMQ = Fluoro Vinyl Methyl Silicone Rubber
- Blend Q = Blend van VMQ and FVMQ

Example 12 -

Synthesis of polymeric adhesive candidate 21 containing carboxylic and methacrylate groups. -- acrylic acid / 1 - (meth) acryloyloxy 2 - hydroxypropylacrylate

5 To a flask were added 14.4g of the 50% solution of polyacrylic acid in water (M.W. 5000), glycidyl methacrylate (40 mmol) and ethanol (30ml). The solution was stirred at 60°C for 4 h. The resulting copolymer was purified via evaporation. The reaction proceeded in  
10 accordance with the following:

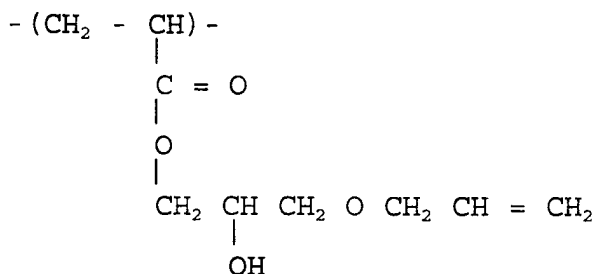
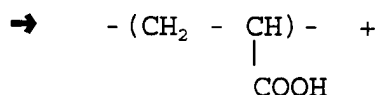
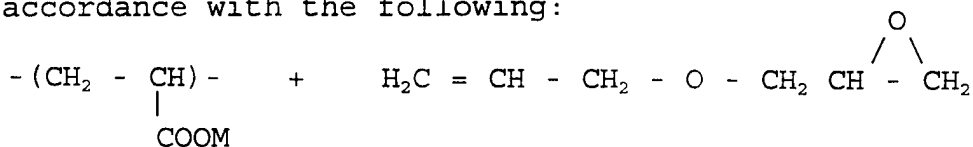


(XIV)

XIII) Example 13 -

Synthesis of polymeric adhesive candidate 22 containing carboxylic and allyl groups - acrylic acid / 1 - allyloxy 2 hydroxypropylacrylate.

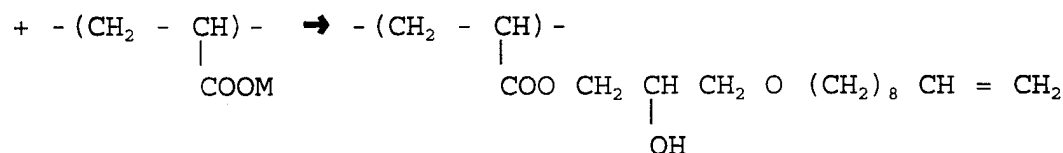
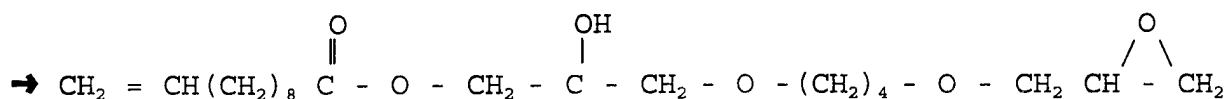
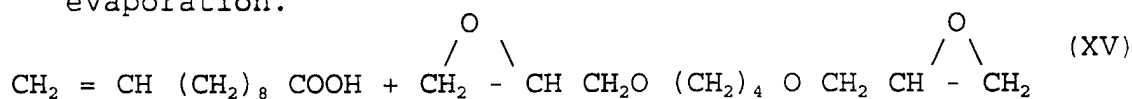
5 To a flask were added 14.4g of the 50% solution of polyacrylic acid in water (M.W. 5000), allyl glycidyl ether (40 mmol) and ethanol (30 ml). The solution was stirred at 60°C for 4 h. The resulting copolymer was purified via evaporation. The reaction proceeded in  
10 accordance with the following:



Example 14 -

Synthesis of polymeric coupling agent 23 containing carboxylic and alkylene groups -- acrylic acid / 1 decenoxy 2-hydroxypropylacrylate.

5 To a flask were added undecenoic acid (100mmol), ethanol (60 ml) and 1,4-butanediol diglycidyl ether (100 mmol). The solution was stirred at 40°C for 2 h, then 28.8 g of a 50% solution of polyacrylic acid in water (M.W. 5000) was added. The mixture was stirred at  
 10 40°C for 2 h. The resulting copolymer was purified via evaporation.



Example 15

In order to demonstrate the efficacy of adhesive candidates 21 and 22, additional adhesion tests utilizing the ISO 5600 procedure was undertaken. EPDM rubber was used as the rubber cylinder interposed between mild steel (MS), stainless steel (SS), aluminum and brass conical insert parts. Results are shown in Table 10.

Table 10. The adhesion strength between EPDM and various metals with coupling agents (CA) as adhesives.

10

Adhesive		Adhesion strength (Newton)			
Code	Conc. (%) <sub>b</sub>	MS	SS	Al	Brass
Blank	0	264	494	465	/
21	5	/	1625	/	895
22	5	1677	1616	1716	1088
23			Z	ZZ	

20

\_\_\_\_\_ The maximum value for 100% rubber failure is 1600-1700 Newton, b: In ethanol.

Z 853.6N 0%R

ZZ 369.3N 0%R

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Example 16 - Durability test of the EPDM-metal adhesion.

In these durability tests, the test pieces were put in an autoclave in water for 4 h. at 110°C under 1 bar overpressure. The adhesion strength was measured according to the method described in Example 2 and the results are shown in Table 11.

Table 11. Durability testing results of EPDM-metal adhesion.

Adhesive Candidate	Adhesion strength (Newton) <sup>a</sup>		
	MS	SS	Al
21	1581	1468	1232
22	1589	1642	1446

a: The maximum value for 100% rubber failure is 1600 - 1700 Newton.

## 2. Discussion of the Invention

In this invention we developed new polymeric coupling agents to adhere elastomers to metals. Normally, the polymeric coupling agents may be applied in a water and/or ethanol solution in a concentration of about 0.1-20wt%, preferably 0.5-10wt%, concentration. The skilled artisan will readily appreciate that molecular weight of the polymer, solubility of the polymer in water and/or ethanol and the final viscosity of polymer solution and the pH of the solution may all be varied depending upon the desired coupling properties of the polymeric coupling agent. The requisite metal may be dip coated or sprayed with the polymeric coupling agent. The substrate is dried for 20 min. at 120°C after which

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the rubber can be molded on the substrate by specific molding processes. Characteristic is that the polymeric coupling agent co-vulcanizes with the elastomer during this proces. One of the advantages over the commercial  
5 coupling agents is that higher cure temperatures can be used and this results in shorter cure times. Another advantage is that the synthesized polymers are water soluble, so environmentally unfriendly solvents are not necessary.

10 The adhesive polymers as referred to above can be prepared by grafting of a specific polymer with requisite chelating and vulcanizable groups. It should be also possible to prepare the polymeric coupling agents by polymerization of monomers having the requisite  
15 chelating and vulcanizable group thereon.

By the terms chelating or chelation, we mean to include functionality that is capable of complexing, sequestering or bonding via coordinate bonds or otherwise with metal atoms or ions including Al, Cu, Fe, etc. On  
20 the other hand, vulcanizable groups, as used herein, include those that bond with elastomer or rubber molecules whether through the formation of chemical crosslinks or otherwise.

Based upon presently available data it is  
25 preferred to utilize either poly(acrylic acid) or polyamine as the backbone, chainforming polymer constituent of the invention. The polyacrylamide polymers were not as successful. In the case of the poly(acrylic acid) the carboxylic acid group provides the  
30 chelation functionality, in the case of polyamine the amine group provides chelation function and is also known to contribute to vulcanization of fluorocarbonrubbers



(FPM). Additional, auxiliary chelation functionality can be provided by further reacting these polymers with, for example, hydroxylamine or chloroacetic acid. In case of the polyamine this is necessary to obtain improved  
 5 adhesion.

In both the poly(acrylic acid) and the polyamine case, the polymers are preferably reacted with allyglycidylether to provide a co-vulcanizable group on the backbone of the polymer. Poly(acrylic acid) can be  
 10 used as adhesive itself, but therefore one need a high molecular weight polymer, typically above 450000 g/mol in this case. The elastomer can probably co-vulcanize with the polymer backbone.

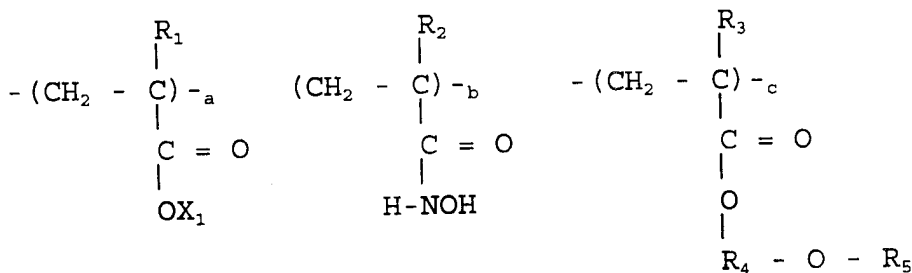
Preferred exemplary polymeric coupling agents therefore  
 15 include:

Precursor	Chelating Group	Vulcanizable Group	Auxillary Group
poly(acrylic acid)	carboxylic acid group from polymer	allyglycidylether	hydroxylamine for chelation
polyamine	amine group from polymer	allyglydicylether	-amine group is a vulcanizable group in case of fluororubbers -iminodiacetic group for additional chelation
polyacrylamide	amide group from polymer	allylamine	allyglycidylether as additional vulcanizable moiety

20

Preferred chelation groups include the carboxylic acid, the hydroxamic acid and the iminodiacetic acid group. Preferred vulcanizable groups are those comprising 1-alkenyl (terminal alkenyl) functionality such as alkenyl (C1-C6) substituted alkylethers. Most preferably such vulcanizable function is provided by reaction of allylglycidylether to the polymer backbone. These polymers can adhere successfully to a variation of metals and rubbers.

At present, adhesives preferred for use which have shown promising efficacy in effecting metal-rubber bonding are those represented by formula:

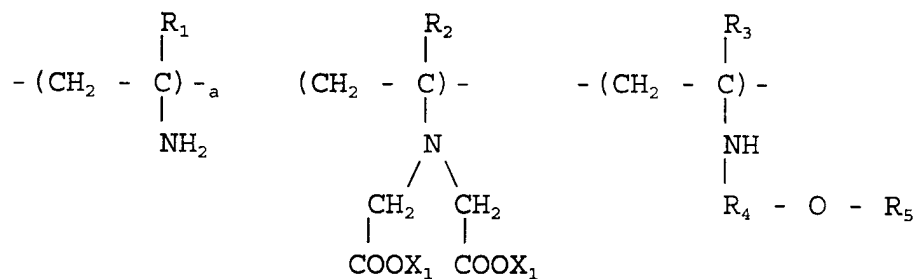


wherein a is present in an amount of 1-99 mol% (based on combined moles of a, b and c present); b, when present, is present in the amount of 1-99 mol% (based on combined moles of a, b and c present); c, when present, is present in the amount of 1-99 mol% (based on combined moles of a, b and c Present), with the provision that either b or c is present. R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> are the same or different and are either H<sub>1</sub> or -CH<sub>3</sub>. X<sub>1</sub> is H or a water and/or ethanol soluble cation such as Na; R<sub>4</sub> is a C<sub>1</sub>-C<sub>4</sub> alkylgroup, or a hydroxy substituted C<sub>1</sub>-C<sub>4</sub> alkyl group, R<sub>5</sub> is C<sub>1</sub>-C<sub>4</sub> alkenyl.

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The molecular weight of the polymeric adhesives in accordance with the invention may span from about 1.000 to about 8-9 million g/mol. These polymers have shown to be especially effective in bonding EPDM - metal substrates.

Other adhesives preferred for use which have shown promising efficacy in effecting metal-rubber bonding are those represented by formula:



wherein a is present in an amount of 1-99 mol% (based on combined moles of a, b and c present); b, when present, is present in the amount of 1-99mol% (based on combined moles of a, b and c present); c, when present, is present in the amount of 1-99mol% (based on combined moles of a, b and c present), with the provision that either b or c is present. R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> are the same or different and are either H or -CH<sub>3</sub>. X<sub>1</sub> is H or a water and/or ethanol soluble cation such as Na; R<sub>4</sub> is a C<sub>1</sub>-C<sub>4</sub> alkylgroup, or a hydroxy substituted C<sub>1</sub>-C<sub>4</sub> alkyl group, R<sub>5</sub> is C<sub>1</sub>-C<sub>4</sub> alkenyl. The molecular weight of the polymeric adhesives in accordance with the invention may span from about 1.0100 to about 8-9 million g/mol. These polymers have shown to be especially effective in bonding FPM - metal substrates.

**SUBSTITUTE SHEET (RULE 26)**

We we have shown and described herein certain  
embodiments of the invention, it is intended that these  
be covered as well any change of modification therein  
which may be made without departing from the spirit and  
5 scope of the invention as defined in the appended claims.

What is claimed is:

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1. Adhesive composition comprising a water or ethanol soluble or dispersible polymeric adhesive, said polymeric constituent having a polymer backbone and a first functional group attached to said backbone, said  
5 first functional group comprising a member selected from the group consisting of i) vulcanizable moieties and ii) chelant moieties adapted to form coordinate bonds with metal atoms or ions; a second functional group attached to said backbone, said second functional group comprising  
10 a member selected from the group consisting of iii) vulcanizable moieties and iv) chelant moieties adapted to form coordinate bonds with metal atoms or ions; with the proviso that said first functional group and said second functional group are different.

2. Adhesive composition as recited in claim 1 wherein said first functional group is a chelant moiety selected from a carboxylic acid moiety, an amide moiety, or an amine moiety.

3. Adhesive composition as recited in claim 1 wherein said polymer comprises polyacrylic acid.

4. Adhesive composition as recited in claim 1 wherein said polymer comprises polyacrylamide.

5. Adhesive composition as recited in claim 1 wherein said polymer comprises polyvinyl amine.

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6. Adhesive composition as recited in claim 2 wherein said second functional moiety is a vulcanizable moiety iii), said vulcanizable moiety iii) comprising an alkenyl radical having a double bond at a terminal carbon atom.

5

7. Adhesive composition as recited in claim 6 wherein said vulcanizable moiety iii) comprises an alkenyl (C<sub>1</sub>-C<sub>6</sub>) substituted or unsubstituted alkyl (C<sub>1</sub>-C<sub>6</sub>) ether.

8. Adhesive composition as recited in claim 7 wherein said substituted or unsubstituted alkyl ether comprises a substituent selected from the group consisting of hydroxyl and oxo moieties.

9. Adhesive as recited in claim 6 wherein said vulcanizable moiety comprises an N-alkenyl (C<sub>1</sub>-C<sub>6</sub>) acrylamide.

10. Adhesive composition as recited in claim 2 wherein said second functional group is a chelant moiety iv), said chelant moiety iv) comprising an N-hydroxysubstituted acrylamido group.

11. Adhesive composition as recited in claim 2 wherein said second functional group is a chelant moiety iv), said chelant moiety iv) comprising an iminodiacetic acid group.

12. Adhesive composition as recited in claim 2 wherein said second functional group is a vulcanizable moiety iii), comprising a N-1-alkenylacrylamido group.

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13. Adhesive composition comprising a water or ethanol soluble or dispersible polymer, said polymer having repeat units I formed from monomers selected from acrylic acid, acrylamide, and vinylamine; and repeat  
5 units II selected from the group consisting of 1) compounds having 1-alkenyl functionality to form a vulcanizable functional moiety, and (2) a chelant compound adapted to form a chelating moiety for forming a coordinate bond with a metal atom or ion.

14. Adhesive composition as recited in claim 13 wherein said chelant compound 2) is present and comprises a member selected from the group consisting of hydroxylamine, chloroacetic acid and chloroacetic anhydride.

15. Adhesive composition as recited in claim 13 wherein said compound 1 is present and comprises a member selected from the group consisting of i) alkenyl glycidyl ethers ii) alkenyl glycidyl (meth) acrylates and iii)  
5 alkenyl amines.

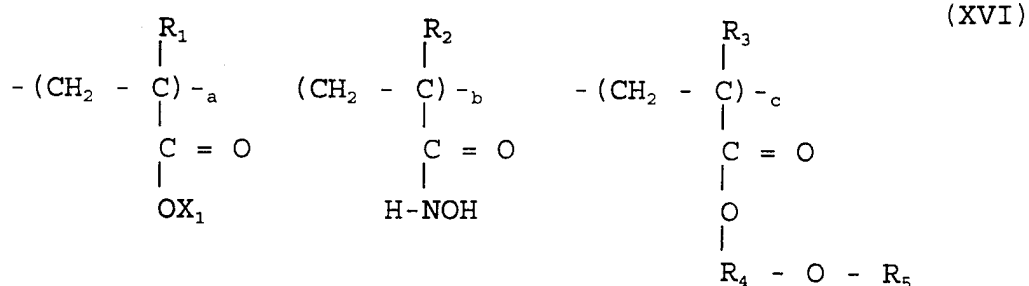
- 46 -

16. Water or ethanol soluble adhesive composition comprising a reaction product of polyacrylic acid and a member selected from the group consisting of (a) and (b) and mixtures of said (a) and (b) wherein (a) is a  
5 compound comprising 1-alkenyl/functionality to form a vulcanizable functional moiety; and  
(b) is a chelant compound adapted to form a chelating moiety upon reaction with said polyacrylic acid, said chelating moiety adapted to form a coordinate bond with a  
10 metal atom or ion.
17. Adhesive composition as recited in claim 16 wherein (a) is present and is allylglycidylether.
18. Adhesive composition as recited in claim 16 wherein (a) is present and is allylamine.
19. Adhesive composition as recited in claim 16 wherein (b) is present and is hydroxylamine.
20. Adhesive composition as recited in claim 16 wherein (a) is present and is allylglycidylether and (b) is present and is hydroxylamine.



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21. Adhesive composition comprising a water or ethanol soluble or dispersible copolymer comprising repeat units having the structure



5 wherein a is present in an amount of 1-99 mol% based on  
 the combined moles of a, b and c present, b, when  
 present, is present in an amount of 1-99 mol% based on  
 the combined moles of a, b, and c present; c, when  
 present is present in the amount of 1-99% mol% based on  
 10 the combined moles of a, b, and c present; with the  
 proviso that at least one of b or c is present;  $R_1$ ,  $R_2$   
 and  $R_3$  are the same or different and are either H or  $\text{CH}_3$ ,  
 $R_4$  is a  $\text{C}_1 - \text{C}_4$  group or a hydroxy substituted  $\text{C}_1 - \text{C}_4$   
 alkyl group,  $R_5$  is  $\text{C}_1 - \text{C}_4$  alkenyl and  $X_1$  is H or a water  
 15 and/or ethanol soluble cation.

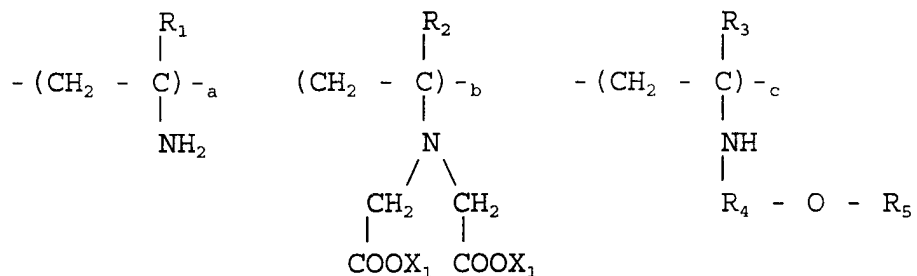
22. Adhesive composition as recited in claim 21  
 wherein (b) is present in an amount of about 10 mol%.

23. Adhesive composition as recited in claim 21  
 wherein (c) is present in an amount of about 10 mol%.

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24. Adhesive composition as recited in claim 21 wherein (b) and (c) are both present with (b) present in an amount of about 10-30 mol% and (c) being present in an amount of about 10-30 mol%; R<sub>4</sub> is 2-hydroxypropyl and R<sub>5</sub> is 1-propenyl.

25. Adhesive composition comprising a water or ethanol soluble or dispersible copolymer comprising repeat units having the structure



wherein a is present in an amount of 1-99mol% (based on the combined moles of a, b, and c present) b, when present, is present in an amount of 1-99 mol% (based on the combined moles of a, b, and c present) and c, when present is present in the amount of 1-99mol% (based on the combined moles of a, b, and c present), with the proviso that either b or c is present, R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> are the same or different and are either H or CH<sub>3</sub>, X<sub>1</sub> is H or a water and/or ethanol soluble cation, R<sub>4</sub> is a C<sub>1</sub>-C<sub>4</sub> alkyl group, R<sub>5</sub> is C<sub>4</sub> alkenyl.

26. Adhesive composition as recited in claim 25 wherein (b) is present in an amount of about 5-10 mol%.

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27. Adhesive composition as recited in claim 25 wherein (c) is present in an amount of about 10 mol%.

28. Adhesive composition as recited in claim 25 wherein (b) and (c) are both present with (b) present in an amount of about 10-30 mol% and (c) present in an amount of about 10-30 mol%.

29. Method of adhering a metal substrate to a rubber substrate comprising contacting one of said substrates with an effective adhesive amount of a water or ethanol soluble or dispersible polymeric adhesive,  
5 said polymeric adhesive comprising a polymer backbone and a first functional group attached to said backbone, said first functional group comprising a member selected from the group consisting of i) vulcanizable moieties and ii) chelant moieties adapted to form coordinate bonds with  
10 metal atoms or ions.

30. Method as recited in claim 29 wherein said first functional group comprises a COOX, chelant moiety, wherein X<sub>1</sub> is H or a water or ethanol soluble cation.

31. Method as recited in claim 29 further comprising a second functional group attached to said backbone, said second functional group comprising a member selected from the group consisting of iii)  
5 vulcanizable moieties and iv) chelant moieties adapted to form coordinate bonds with metal atoms or ions; with the proviso that said first functional group and said second functional group are different; and placing said substrate together with said adhesive interposed  
10 therebetween to effect said adhering.

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32. Method as recited in claim 31 wherein said first functional group is a chelant moiety ii selected from a carboxylic acid moiety, an amide moiety, or an amine moiety.

33. Method as recited in claim 31 wherein said polymer comprises polyacrylic acid.

34. Method as recited in claim 31 wherein said polymer comprises polyacrylamide.

35. Method as recited in claim 31 wherein said polymer comprises polyvinyl amine.

36. Method as recited in claim 32 wherein said second functional group is a vulcanizable moiety iii, said vulcanizable moiety iii) comprising an alkenyl radical having a double bond at a terminal carbon atom.

37. Method as recited in claim 36 wherein said vulcanizable moiety comprises an alkenyl (C<sub>1</sub>-C<sub>6</sub>) substituted or unsubstituted alkyl (C<sub>1</sub>-C<sub>6</sub>) ether.

38. Method as recited in claim 32 wherein said substituted or unsubstituted alkyl comprises a substituent selected from a group consisting of hydroxy and oxo substituents.

39. Method as recited in claim 32 wherein said second functional group is a vulcanizable moiety iii) comprising an N-alkenyl (C<sub>1</sub>-C<sub>6</sub>) acrylamide.

40. Method as recited in claim 32 wherein said second functional group comprises a chelant moiety iv) comprising an N-hydroxysubstituted acrylamide group.

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41. Method as recited in claim 32 wherein said second functional group comprises a chelant moiety iv) comprising an iminodiacetic acid group.
42. Method as recited in claim 32 wherein said second functional group comprises a vulcanizable group iii) comprising a N-1-alkenylacrylamido group.
43. Method as recited in claim 31 wherein said adhesive is present in said water or ethanol in an amount of about 1-20% weight.
44. Method as recited in claim 43 wherein said contacting comprises spraying said adhesive onto one of said substrates.
45. Method as recited in claim 43 wherein said contacting comprises dipping one of said substrates into said water or ethanol containing said adhesive.
46. Method as recited in claim 43 further comprising after said contacting, heating said adhesive.

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47. Method of adhering a metal substrate to a rubber substrate comprising contacting one of said substrates with an ethanol or water based dispersion or solution comprising an adhesive comprising a polymer  
5 having repeat units I formed from monomers selected from acrylic acid, acrylamide, and vinylamine and repeat units II selected from the groups consisting of (a) and (b) wherein (a) is a compound comprising 1-alkenyl  
10 functionality to form a vulcanizable functional moiety, and (b) is a chelant compound adapted to form a chelating moiety for forming a coordinate bond with a metal atom or ion from said metal substrate; and placing said substrates together with said adhesive interposed therebetween to effect said adhering.

15 48. Method as recited in claim 47 wherein said compound (b) is present and comprises a member selected from the group consisting of hydroxylamine, chloroacetic acid and chloroacetic anhydride.

49. Method as recited in claim 48 wherein said compound (a) is present and comprises a member selected from the group consisting of i) alkenyl glycidyl ethers  
5 ii) alkenyl glycidyl (meth) acrylates and iii) alkenyl amines.

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50. Method of adhering a metal substrate to a rubber substrate comprising contacting one of said substrates with a water or ethanol solution or dispersion comprising from about 1-20 wt% of a polymeric rubber to metal adhesive, said adhesive comprising a reaction product of polyacrylic acid and a member selected from the group consisting of (a) and (b) and mixtures of (a) and (b) wherein (a) is a compound comprising a-alkenyl functionality to form a vulcanizable functional moiety with said rubber and (b) is a chelant compound adapted to form a chelating moiety upon reaction with said polyacrylic acid, said chelating moiety adapted to form a coordinate bond with a metal atom or ion from said metal substrate; said method further comprising placing said substrates together with said adhesive interposed therebetween to effect said adhering.

51. Method as recited in claim 50 wherein (a) is present and is allyglycidylether.

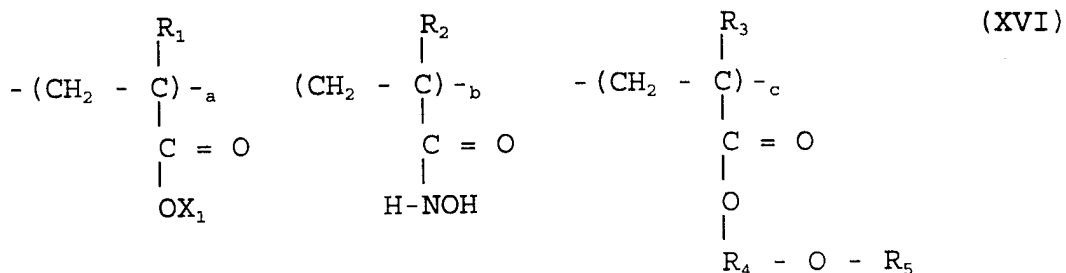
52. Method as recited in claim 50 wherein (a) is present and is allylamine.

53. Method as recited in claim 50 wherein (b) is present and is hydroxylamine.

54. Method as recited in claim 50 wherein (a) is present and is allyglycidylether and (b) is present and is hydroxylamine.

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55. Method of adhering a metal substrate to a rubber substrate comprising contacting one of said substrates with a water or ethanol solution or dispersion comprising a water or ethanol soluble or dispersible copolymer comprising repeat units having the structure



wherein a is present in an amount of 1-99 mol% based on the combined moles of a, b and c present, b, when present, is present in an amount of 1-99 mol% based on the combined moles of a, b, and c present; c, when present is present in the amount of 1-99% mol% based on the combined moles of a, b, and c present; with the proviso that at least one of b or c is present; R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> are the same or different and are either H or CH<sub>3</sub>, R<sub>4</sub> is a C<sub>1</sub> - C<sub>4</sub> group or a hydroxy substituted C<sub>1</sub> - C<sub>4</sub> alkyl group, R<sub>5</sub> is C<sub>1</sub> - C<sub>4</sub> alkenyl and X<sub>1</sub> is H or a water and/or ethanol soluble cation.

56. Method as recited in claim 55 wherein said adhesive composition (b) is present in an amount of about 10 mol%.

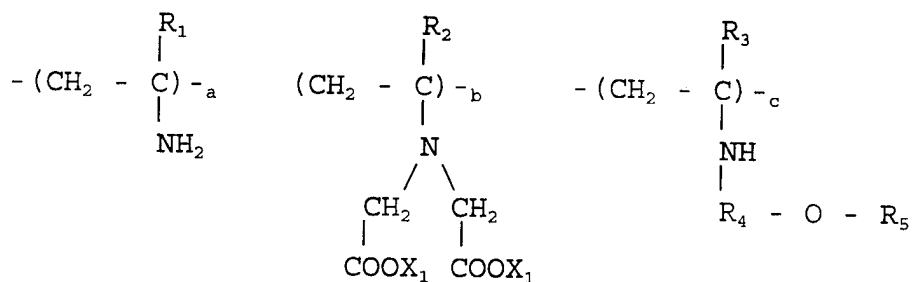
57. Adhesive composition as recited in claim 55 wherein (c) is present in an amount of about 10 mol%.

58. Adhesive composition as recited in claim 55 wherein (b) and (c) are both present with (b) present in an amount of about 10-30% mol% and (c) being present in an amount of about 10-30 mol%; R<sub>4</sub> is 2-hydroxypropylacrylate and R<sub>5</sub> is 1-propenyl.



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59. Method of adhering a metal substrate to a rubber substrate comprising contacting said substrates with a water or ethanol solution or dispersion comprising a water or ethanol soluble or dispersible copolymer comprising repeat units having the structure



- wherein a is present in an amount of 1-99 mol% (based on the combined moles of a, b, and c present) b, when present, is present in an amount of 1-99 mol% (based on the combined moles of a, b, and c present) and c, when present, is present in the amount of 1-99 mol% (based on the combined moles of a, b, and c present), with the proviso that either b or c is present, R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> are the same or different and are either H or CH<sub>3</sub>, X<sub>1</sub> is H or a water and/or ethanol soluble cation, R<sub>4</sub> is a C<sub>1</sub>-C<sub>4</sub> alkyl group, or a hydroxy substituted C<sub>1</sub>-C<sub>4</sub> alkyl group, R<sub>5</sub> is C<sub>1</sub>-C<sub>4</sub> alkenyl.

60. Method as recited in claim 59 wherein (b) is present in an amount of about 5-10 mol%.

61. Method as recited in claim 60 wherein (c) is present in an amount of about 10 mol%.

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62. Method as recited in claim 60 wherein (b) and (c) are both present with (b) present in an amount of about 10-30 mol% and (c) present in an amount of about 10-30 mol%.

INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US97/22657

**A. CLASSIFICATION OF SUBJECT MATTER**  
 IPC(6) :C08F 8/00, 8/32; C09J 4/00  
 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. : 156/327; 525/327.3, 327.6, 327.7, 328.2, 329.6, 329.7, 329.9; 526/271, 273, 304

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)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4,762,866 A (SHIH et al) 09 August 1988.	1-62
A	US 4,426,243 A (BRIGGS) 17 January 1984.	1-62
A	US 3,980,663 A (GROSS) 14 September 1976.	1-62
A	US 3,284,423 A (KNAPP) 08 November 1966.	1-62

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
*E* earlier document published on or after the international filing date	*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
*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)	*Z* 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 04 MARCH 1998	Date of mailing of the international search report 13 MAR 1998
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230	Authorized officer B. Lipman BERNARD LIPMAN Telephone No. (703) 308-0661

**INTERNATIONAL SEARCH REPORT**

International application No.  
PCT/US97/22657

**A. CLASSIFICATION OF SUBJECT MATTER:**

US CL :

156/327; 525/327.3, 327.6, 327.7, 328.2, 329.6, 329.7, 329.9; 526/271, 273, 304