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**WO 01/51577 A2**

(54) Title: OPTIMIZED ANAEROBIC ADHESIVE COMPOSITIONS AND METHODS OF PREPARING SAME

(57) Abstract: The present invention relates to anaerobic adhesive compositions which have been optimized using experimental design techniques to produce desired physical properties. A simplified cure system is disclosed which permits enhanced fixture and cure times.

**OPTIMIZED ANAEROBIC ADHESIVE COMPOSITIONS**  
**AND METHODS OF PREPARING SAME**

**FIELD OF THE INVENTION**

The present invention relates to anaerobic adhesive compositions which have been optimized to produce desired physical properties. Methods of producing optimized compositions using experimental design techniques are also disclosed.

5

**BACKGROUND OF RELATED TECHNOLOGY**

Anaerobic adhesive compositions are well known for their ability to remain in a liquid, unpolymerized state in the presence of oxygen and to cure to a solid state upon 10 the exclusion of oxygen. Early work on anaerobic adhesive compositions concentrated on developing a cure system which improved the speed and/or bond strength of the adhesive composition. Various cure systems for anaerobic adhesive compositions have been developed to primarily focus on efficiently performing the redox reaction, which is the basis for anaerobic chemistry. Hydroperoxides were found to serve as a catalyst 15 for the generation of a free radical. For example, U.S. Patent No. 2,895,950 to Kriebel, discloses the inclusion of hydroperoxides in amounts of 0.1 to 10% by weight in anaerobic adhesive compositions to achieve faster cure times. Amines, used in amounts up to about 10% by weight, are also disclosed in the '950 patent as accelerators to generate free radicals of the peroxide.

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Various accelerator compounds, such as tertiary amines, imides, polyamines, cyclicamines and arylamines, have been successfully included in anaerobic adhesive compositions to further increase cure speeds and completion of cure. See, e.g., U.S. Patent No. 3,041,322 (tertiaryamines), U.S. Patent No. 3,046,282 (imides), U. S. Patent 25 No. 3,203,941 (polyamines), and U.S. Patent No. 3,218,305 (cyclic and arylamines), all to Kriebel. These accelerators were generally used in amounts of about 0.05 up to about 20%, depending on the type of amine and amount of peroxide present in the anaerobic adhesive composition. Ordinarily, according to Kriebel, the amount of

accelerator present was significantly less than the peroxide. Additionally, no teaching or suggestion is present in these patents of using specific relative amounts of peroxide to reducing agents.

5        Those persons of ordinary skill in the art acknowledge that peroxides serve as a free radical generating source which initiate free radical curing of the polymerizable anaerobic adhesive monomer compositions. To increase the speed at which the free radical is generated, accelerators are employed in combination with the peroxides to enhance the speed at which the peroxide free radical is generated. In so doing, the cure  
10      speed of the anaerobic adhesive composition is increased.

As anaerobic adhesive compositions have evolved, various combinations of peroxides and accelerators have been used. Recently, such compositions have employed a plurality of compounds as accelerators to serve as reducing agents for the  
15      peroxide to increase cure speed. The virtually infinite number of possible combinations of individual components and their relative amounts, have made formulating anaerobic adhesive compositions a complex exercise depending on the properties sought for the composition. While many current anaerobic adhesive compositions exhibit the ability to rapidly polymerize, optimum compositions for a desired set of properties has not  
20      been predictable. Thus, given the large number of potential combinations and permutations of anaerobic adhesive composition variables for a given set of desired properties, optimization has neither been practical nor achievable.

U.S. Patent Nos. 4,287,330 and 4,321,349 to Rich disclose anaerobic adhesive  
25      compositions which include a hydrazine accelerator, along with peroxides and amines in amounts previously referred to herein, to increase the cure speed of the anaerobic curing monomer. The hydrazines are disclosed as being useful in amounts of about 0.1-5% by weight. No disclosure is found in the '330 and '349 patents with regard to achieving faster cure speed by adjusting the specific relative amounts of peroxide,  
30      hydrozine and amine. Anaerobic adhesive compositions have also conventionally employed primer compositions to speed their cure. On substrates such as stainless steel, zinc, dichromate, and cadmium, which are considered "slow" or relatively

inactive materials for anaerobic cure, primer compositions have been considered necessary for quick fixture and cure times required of many applications.

5        The use of primer compositions requires an additional step prior to applying the anaerobic adhesive composition, which is often inconvenient and costly. Often the solvent used to carry the accelerator component in the primer is environmentally harmful and requires special handling and disposal. Moreover, ordinarily the user must wait until the solvent has evaporated before applying the adhesive.

10        Designed experimentation (DOE) techniques are known as a method of evaluating multiple factors during scientific experimentation. DOE techniques often use an artificial intelligence component known as a neural network. This technique uses software-generated models to systematically consider the extent to which different variable factors interact by considering many factors simultaneously, while conducting 15        fewer experiments. Commercially available software, such as CAD/CHEM offered by Computer Associates, International, Ilandia, NY, produces models to predict the outcome for any given combination of factors. DOE techniques provide a way to combine such factors for products, processes and designing optimized compositions. It is not believed that DOE techniques have been applied to the optimization of anaerobic 20        adhesive compositions. Instead, conventional one-factor-at-a-time (OFAT) techniques have been a common method of learning about the characteristics and improving upon the properties of anaerobic adhesive compositions.

25        Whereas the Kriebel patents disclosed anaerobic adhesive compositions with relatively few components, current commercially available anaerobic adhesive compositions include many additional components which are believed to participate in the cure mechanism. The ability to determine optimized compositions which are reduced to the least number of components would represent a significant advance in achieving desired properties, as well as representing significant simplification in the 30        manufacturing process, reduction in the material cost and an increase in overall production efficiency. It would be further advantageous if such optimized compositions achieve faster fixture and cure times without the need for independent primer compositions or numerous accelerator combinations. Moreover, there is a need

for a method of generating an optimized composition based on a set of desired properties of the adhesive, whether these properties be in the uncured or cured form, or in the cure profile.

## 5 SUMMARY OF THE INVENTION

The present invention provides anaerobic adhesive compositions, reaction products of which demonstrate improved initial room temperature torque strength on an oxidizable element, which element participates in curing the composition through its 10 oxidation. The inventive compositions include:

- a.) at least one anaerobically curable (meth)acrylate monomer;
- b.) a cure system for the (meth)acrylate monomer comprising:
  - (i) at least one free radical generating material; and
  - (ii) an acidic reducing agent for the free radical generating material, each of (i) and (ii) being present in substantially equal amounts; and
  - (iii) an accelerator for the reduction of the free radical generating material.

20 The cure system is present in an amount sufficient to achieve about 30% or more of its 24 hour cure strength in about 5 minutes or less. The inventive composition is free of maleic acid in the amount of 0.1 to 1% by weight of the total composition.

25 In one aspect of the present invention there is provided for optimized anaerobic adhesive compositions which can develop a significant portion of their ultimate physical strength in substantially shorter times when compared to known anaerobic adhesive compositions. Compositions of the present invention also exhibit extremely fast fixture or set times when compared to known anaerobic adhesive compositions. 30 These and other advantages are achieved using fewer components than previously thought possible.

Certain components in the anaerobic adhesive composition previously thought to be necessary, such as the use of multiple accelerators, have now been eliminated. Notwithstanding the plethora of prior anaerobic adhesive compositions known to those skilled in the art, the ability to achieve exceedingly fast fixture time and reach 5 significant strength in a few minutes, in the absence of substrate primers has previously been unobtainable. Conventional methods of increasing fixture time or cure speed has required the use of substrate primers which include accelerator compounds for enhancing cure speed.

10 The present invention provides optimized anaerobic adhesive compositions which have a reduced number of components, yet which achieve the aforementioned advantages without the need for either the application of an independent primer composition, or a plurality of accelerating components. The reduction of components necessary for the anaerobic adhesive composition to cure provides the additional 15 advantages of reduced material cost and increased convenience and overall manufacturing efficiency as compared to commercially known compositions.

In a further aspect of the invention there is provided an anaerobic adhesive composition which includes the following components:

20

- a.) at least one anaerobically curable alkyl (meth)acrylate monomer present in amounts of less than 60% by weight of the total composition;
- b.) a cure system for said (meth)acrylate monomer comprising:

25

- (i) at least one free radical generating material;
- (ii) an acidic reducing agent for said free radical generating material, each of (i) and (ii) being present in substantially equal amounts; and
- (iii) an accelerator for the reduction of said free radical generating material;

30

wherein said cure system is present in an amount sufficient to achieve about 30% or more of its 24 hour cured torque strength in about 5 minutes or less.

In still a further aspect of the invention there is provided a method of bonding substrates which includes the steps of combining in admixture:

5 (i) at least one anaerobically curable (meth)acrylate monomer;  
(ii) at least one free radical generating material;  
(iii) an acidic reducing agent for said free radical generating material, each of  
(i) and (ii) being present in substantially equal amounts; and  
(iv) an accelerator for the reduction of said free radical generating source.

10

wherein said anaerobic composition is free of maleic acid in the amount of 0.1 to 1.0% by weight of the total composition.

15 Methods of preparing and optimizing such anaerobic adhesive compositions are also disclosed. In particular, the use of DOE techniques which incorporate artificial intelligence components produce optimized compositions having properties heretofore not believed possible. Thus, in another aspect of the invention there is a method for optimizing an adhesive composition to produce a set of desired properties. The method includes the steps of:

20

a.) providing in a machine readable storage medium a data set of adhesive composition components;  
b.) generating a statistically validated experimental design model comprising a set of adhesive compositions representing independent variables;  
c.) generating objective test data of the set of adhesive composition from step b.), the test data results representing a set of dependent variables; and  
d.) establishing a correlation between the independent and dependent variables.

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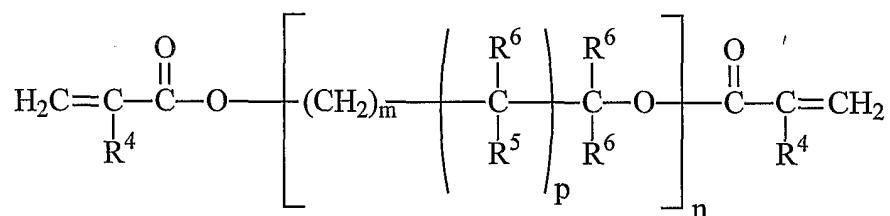
Carrying out the steps of this method produces an optimized composition for the physical properties desired.

### DETAILED DESCRIPTION OF THE INVENTION

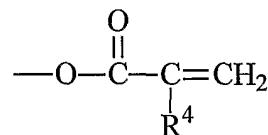
Curable polyolefinically unsaturated monomers may be used as the 5 polymerizable, crosslinkable resin component including acrylic and methacrylic resins, and mixtures thereof. The term (meth)acrylic is used to refer to both types of resins.

Useful anaerobic curing monomers include the alkylene glycol diacrylates having the general formula:

10



wherein  $\text{R}^4$  is selected from the group consisting of hydrogen, halogen, and lower alkyl of 1-4 carbon atoms;  $\text{R}^5$  is selected from the group consisting of hydrogen, -OH and



15

$\text{R}^6$  is a radical selected from the group consisting of hydrogen, lower alkyl of 1-4 carbon atoms, hydroxyalkyl of 1-4 carbon atoms, and  $m$  is an integer equal to at least 1, desirably 1-8 and more desirably from 1 to 4;  $n$  is an integer equal to at least 1, desirably, 1 to 20; and  $p$  is 0 or 1.

20

Typical of these monomers are mono-, di-, tri- tetra- and polyethylene glycol dimethacrylate and the corresponding diacrylates; di(pentamethylene glycol) dimethacrylate; tetraethylene glycol di(chloroacrylate); diglycerol diacrylate; diglycerol tetramethacrylate; butylene glycol dimethacrylate; neopentyl glycol diacrylate; and 25 trimethylopropane triacrylate.

Particularly useful polymerizable crosslinkable components are ethoxylated trimethylolpropane triacrylate, trimethylol propane trimethacrylate, dipentaerythritol monohydroxypentacrylate, pentaerythritol triacrylate, ethoxylated trimethylolpropane triacrylate, 1,6-hexanedioldiacrylate, neopertyl glycoldiacrylate, pentaerythritol tetraacrylate, 1,2-butylene glycoldiacrylate, trimethylolpropane ethoxylate tri(meth)acrylate, glycetyl propoxylate tri(meth)acrylate, trimethylolpropane tri(meth)acrylate, dipentaerythritol monohydroxy penta(meth)acrylate, tri(propylene glycol) di(meth)acrylate, neopentylglycol propoxylate di(meth)acrylate, 1,4-butanediol di(meth)acrylate, polyethyleneglycol di(meth)acrylate, triethyleneglycol di(meth)acrylate, butylene glycol di(meth)acrylate, ethoxylated bisphenol A di(meth)acrylate and combinations thereof.

Various useful urethane-acrylate type monomers, such as those described in U.S. Patent No. 3,925,988 to Gorman, and U.S. Patent No. 4,309,526 to Baccei, each of which are incorporated herein by reference may be used. The monomers disclosed in the '526 patent may be viewed as one-component polymerizable block copolymers (prepolymers) having rigid and flexible segments. This is achieved by the chemical linking of precursor "prepolymers" which are subsequently "capped" with (meth)acrylate, functionality.

Other useful monomers include those acrylates derived from bisphenol-A, such as bisphenol-A dimethacrylate, hydrogenated bisphenol-A dimethacrylate, and ethoxylated bisphenol-A dimethacrylate.

25

While di- and other polyacrylate esters have been found particularly desirable, monofunctional acrylate esters (esters containing one acrylate group) also may be used. When dealing with monofunctional acrylate esters, it is desirable to use an ester which has a relatively polar alcoholic moiety. Such materials are less volatile than low molecular weight alkyl esters and, more importantly, the polar group tends to provide intermolecular attraction during and after cure, thus producing more desirable cure properties, as well as a more durable sealant or adhesive. Particularly desirable are the polar groups selected from labile hydrogen, heterocyclic ring, hydroxy, amino, cyano,

and halogen polar groups. Useful examples of compounds within this category include cyclohexyl methacrylate, tetrahydrofurfuryl methacrylate, hydroxyethyl acrylate, hydroxypropyl methacrylate, t-butylaminoethyl methacrylate, cyanoethylacrylate, and chloroethyl methacrylate. The materials are often incorporated as reactive diluents  
5 which are capable of copolymerizing with the various other polymerizable materials.

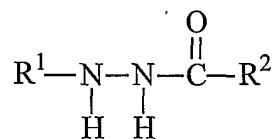
Other unsaturated reactive diluents, such as styrene and acrylonitrile, can also be used. When used, the concentration of such diluents should be less than about 60 percent by weight, and preferably about 40 to about 10 percent by weight of the  
10 composition, based on the total weight of the composition.

The optimized anaerobic adhesive compositions of the present invention include a simplified cure system which serves to room temperature cure anaerobic monomer compositions at speeds significantly faster than known compositions containing some  
15 of the same type of components.

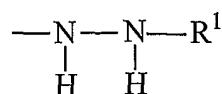
The simplified cure systems of the present invention may be comprised of three components: a peroxide free radical initiator; a reducing agent for the initiator; and an accelerator for the initiator. It has been determined that to achieve the aforementioned  
20 advantages of the present invention, the relative amounts of free radical initiator to reducing agent is desirably substantially the same. Additionally, the relative amount of accelerator is desirably about half that of the free radical initiator component.

A number of well known initiators of free radical polymerization may be  
25 incorporated in the present invention. Among those include, without limitation, hydroperoxides, such as cumene hydroperoxide (CHP), paramenthane hydroperoxide, tertiary butyl hydroperoxide (TBH) and tertiary butyl perbenzoate. While the useful amounts of peroxide compounds typically range from about 0.1 to about 10% by weight of the total composition, the present invention achieves its speed of cure when  
30 about 1% by weight of the peroxide is used along with a substantially equal amount of the reducing agent, e.g., saccharin. Thus, for the cure speed advantages discussed herein, the ratio of peroxide to peroxide reducing agent (e. g., saccharin) is desirably about 1:1, and the ratio of peroxide to accelerator is desirably about 2:1.

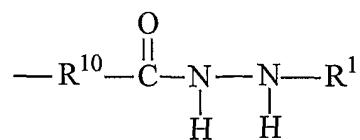
Useful accelerators for the present invention include compounds having the following formula:



5 wherein  $\text{R}^1$  is selected from alkyl from 2 to 6 carbon atoms, cycloalkyl, aryl, alkenyl, and cycloalkenyl and  $\text{R}^2$  is selected from hydrogen, alkyl, cycloalkyl, alkenyl and cycloalkenyl, aryl, alkoxy, aryloxy, carbonyl, amino, and the following groups:



and



10

wherein  $\text{R}^{10}$  is selected from alkyl groups containing one to about 10 carbon atoms, alkenyl groups containing two to about 10 carbon atoms, and aryl groups containing up to about 10 carbon atoms. Examples of useful accelerator compounds include 1-acetyl-2-phenyl hydrazine, 1-acetyl-2(p-tolyl) para-toluene sulfonyl hydrazide, 15 1-formyl-2-phenyl hydrazine and combinations thereof. As previously noted, the ratio of peroxide to accelerator is desirably about 2:1. While the amount of accelerator can be proportionately varied to the amount of peroxide present, to achieve the aforementioned desired physical properties of the anaerobic adhesive composition the accelerator is desirably present in about 0.5% by weight of the total composition.

20

Stabilizers and inhibitors may also be employed as well as chelating agents to control and prevent premature peroxide decomposition and polymerization. Among those useful inhibitors include phenols such as hydroquinone and quinones. Chelating agents may be used to remove trace amounts of metal contaminants. An example of a

useful chelating agent is the tetrasodium salt of ethylenediamine tetraacetic acid (EDTA).

Other agents such as thickeners, plasticizers, fillers, elastomers, thermoplastics, 5 and other well-known additives may be incorporated where functionally desirable.

The DOE method used to optimize the compositions of the present invention includes first choosing a series of components and their relative ranges and entering them into a DOE software program, such as the commercially available program 10 CAD/CHEM. The data entered represent independent variable data sets which represent potential anaerobic compositions from which an optimized composition will be determined. A statistically validated model is then generated for a given set of physical properties. Selected compositions are chosen for physical testing based on the desired properties previously identified. The results of physical testing are then fed into 15 the computer and a neural network is used to correlate the test data with the adhesive compositions. The neural network uses a multilayered approach that approximates complex mathematical functions to process data. It consists of many processing elements or nodes that work in parallel. Nodes are connected to each other in layers and layers are interconnected. These nodes are mathematical functions. The 20 connections between these nodes, which weight the data transformation from each node and send the information to the next node, are how the neural network "learns" or "thinks". The neural network is trained by real-life examples of data called training sets. The neural network creates connections and learns patterns based on these training sets. The network adapts to changing inputs and learns trends from data. A set 25 of real-life examples, such as the physical data from a chosen anaerobic adhesive composition is entered into the neural network, which then weighs the connections between nodes based on each training example. Each connection weight builds on previous decision nodes which propagate to a final decision or outcome. As a final decision approaches, the network compares its answer against an answer in a training 30 set. If there is a match, within a predefined tolerance, the neural network stores these connection weights as successful. If the decision outcome is outside a given tolerance level, the network cycles through the training set again.

Among various useful neural networks are back propagation neural networks, feed forward networks, radial basis function networks and probabilistic neural networks.

5        Objective test data which can be fed into the neural network and correlated with the adhesive compositions include physical strength data, stability data, heat resistance data, cure speed data, viscosity data, solvent resistance data, cure through gap data, thermal expansion data, toughness data, solubility data, density data, modulus data, Tg, heat aging data and combinations thereof. Among the strength data useful for  
10      optimizing anaerobic adhesive compositions are torque data, tensile data, shear data, compression data, elongation data, impact data and combinations thereof.

15      The method of optimization of the present invention is useful on various adhesive compositions in addition to anaerobic adhesive compositions. For example, the method may be used to optimize cyanoacrylate, silicone, epoxy and acrylic adhesive compositions.

### EXAMPLES

20      The following optimized anaerobic composition was prepared in accordance with the following method of the present invention. To begin, a series of components and their relative amount ranges were defined. These represent potential anaerobic compositions, from which optimized compositions can be determined. Among the physical properties sought after were improved fixture or set time, the ability to develop  
25      greater strength more rapidly, as well as high ultimate cure strength. It is understood that final optimized compositions may or may not use all of the possible components listed. Rather, the components represent sets of data choices which are used to create an anaerobic adhesive composition model.

30      A matrix of potential anaerobic composition components and their relative amount ranges was established. This matrix was modeled using a commercially available DOE program known as CAD/CHEM. The components in this model are independent variables. The DOE software program statistically validates these models.

Selected compositions are chosen for physical testing based on the desired properties previously identified by statistical analysis in the DOE software. The results of physical testing represent dependent variables which are then fed into the computer and correlated with the adhesive compositions to predict and extrapolate optimized properties for compositions not tested. Queries as to the best composition for a desired physical property can be input into the software and a predicted result is provided. Queries can also be entered to request a predicted physical property for a desired composition. For example, the DOE uses neural networks to learn and refine optimization of a given composition. Optimized compositions were obtained in this manner for enhanced cure speed and fixture time. The neural network correlated the physical test results with the anaerobic adhesive compositions to generate an optimized composition designed with the desired physical properties and cure profile.

The objective test data which can be measured for use with DOE techniques includes physical strength data, stability data, heat resistance data, cure speed data, viscosity data, solvent resistance data, cure through gap data, thermal expansion data, toughness data, solubility data, density data, modulus data, Tg, heat aging data and combinations thereof. Of particular significance in adhesive compositions is strength data, such as torque data, tensile data, shear data, compression data, elongation data, impact data and combinations thereof. Other physical properties such as stability and shelf life data may also be used in the present optimization method.

In addition to anaerobic adhesive compositions, the optimization method of the present invention may also be used to optimize cyanoacrylate adhesives, silicone adhesives, epoxy adhesives, acrylic adhesives and the like.

As a result of the above design experiment, an optimized anaerobic composition was generated having the following compositions:

**INVENTIVE COMPOSITION 1**

30

COMPONENT	% WEIGHT
Monomers PEGMA <sup>1</sup>	20.70

EBIPMA <sup>2</sup>	72.35
Cure System	
Cumene Hydroperoxide	1.0
Saccharin	1.0
APH <sup>3</sup>	0.5
Other Additives	
Stabilizers, Chelators, Dyes, Thickeners	4.45
Total	100.00

<sup>1</sup>polyethylene glycol dimethacrylate

<sup>2</sup>ethoxylated bisphenol A dimethacrylate

<sup>3</sup>1-acetyl 2-phenyl hydrazine

As a result of optimization, numerous cure components were omitted from the  
5 current commercial product and the relative percentages of the cure system components  
were adjusted to yield the desired properties.

The above inventive composition can be compared with Loctite Threadlocker  
243, a commercially available anaerobically curable composition. Loctite  
10 Threadlocker 243 has a composition with the following parameters:

**COMMERCIALLY AVAILABLE LOCTITE THREADLOCKER 243**

Component	% by Weight
PEGMA	60-65
PGDOA <sup>1</sup>	20-25
Poly(vinyl acetate)	5-10
Poly (ethylene)	3-5
Cumene Hydroperoxide	1-3
Castor Oil Derivative	1-3
Modified Silicon Dioxide	1-3
Saccharin	1-3
APH	0.1-1
Maleic Acid	0.1-1

<sup>1</sup> polyglycol dioctanoate

5 Inventive Composition 1 was tested for room temperature torque strength on nuts and bolts made of various metals. The nuts were pretorqued on the bolts and tested in accordance with DIN 54454. These torque strengths were compared against Loctite Threadlocker 243 and the results are tabulated below. As noted from the tables, the amount of torque strength, as measured by inch-pounds, varies depending on the metal used. Certain metals, such as steel, copper or copper-containing alloys such as brass, are considered highly active surfaces because they accelerate the cure speed of anaerobic adhesive compositions. These compositions develop a greater portion of their final cure strength early on in the polymerization process. On less active surfaces, including stainless steel, zinc dichromate and cadmium, cure speeds are slower and the 10 compositions take longer to develop their cure strength. Often final cure strengths on these surfaces are lower than an active substrate.

15

It is apparent from each of Tables 1-4, that Inventive Composition 1 exhibited significantly higher initial-break torque values at room temperature than the 20 commercial anaerobic adhesive product Loctite Threadlocker 243, regardless of the type of metal used for nuts and bolts. Significantly higher physical strengths were achieved by the inventive compositions at each of the time intervals tested. It is

generally understood by persons of ordinary skill in the art of anaerobic chemistry that full cure is reached after 24 hours at room temperature.

5      Table 1  
Initial-Break Room Temperature Torque Values (Inch-Pounds) on Degreased Steel  
Nuts and Bolts

	5 min.	10 min.	30 min.	1 hour	24 hours
Inventive Composition 1	81	90	149	179	283
Threadlocker 243*	40	45	74	115	225

10

Table 2  
Initial-Break Room Temperature Torque Values (Inch-Pounds) on Reoiled Steel  
Nuts and Bolts

	5 min.	10 min.	30 min.	1 hour	24 hours
Inventive Composition 1	45	50	86	90	213
Threadlocker 243*	39	44	53	56	113

15

20      Table 3  
Initial-Break Room Temperature Torque Values (Inch-Pounds) on Zinc Nuts and Bolts

	5 min.	10 min.	30 min.	1 hour	24 hours
Inventive Composition 1	44	51	60	67	80
Threadlocker 243*	37	39	50	72	131

Table 4  
Initial-Break Room Temperature Torque Values (Inch-Pounds) on Stainless Steel  
Nuts and Bolts

	5 min.	10 min.	30 min.	1 hour	24 hours
Inventive Composition 1	44	58	67	79	167
Threadlocker 243*	36	35	45	83	157

5

Table 5 below shows that the inventive compositions achieve a significantly greater percent of their ultimate physical strength within the first 5 minutes, as compared to Loctite 243\*.

10

Percent of 24 Hour Cure Torque Strength Reached For A Given Time Interval

		<u>INVENTIVE COMPOSITION 1</u>	<u>Loctite 243</u>
	<u>Degreased Steel*</u>		
15	5 min.	28.6%	17%
	10 min.	31.8%	20%
	30 min.	52.6%	32%
	1 hour	63%	51%
	<u>Reoiled Steel*</u>		
20	5 min.	21%	34%
	10 min.	23%	38%
	30 min.	40%	46%
	1 hour	42%	49%
25	<u>Stainless Steel*</u>		
	5 min.	26%	22%
	10 min.	34%	22%
	30 min.	40%	28%
	1 hour	47%	52%
30	<u>Zinc*</u>		
	5 min.	55%	28%
	10 min.	63.75%	29.8%
	30 min.	75%	38%
35	1 hour	83.75%	55%

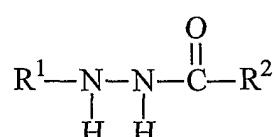
\*nuts and bolts were pretorqued in accordance with DIN 54454

The data set forth above demonstrates that in about 5 minutes or less, the inventive anaerobic adhesive compositions reach about 30% or more of their ultimate torque strength on substrates such as degreased steel and as much as 55% of its ultimate torque strength on zinc. On substrates such as reoiled steel, the inventive composition 5 exhibits significantly enhanced speed of cure and ultimate torque strength as compared to Loctite Threadlocker 243. Table 2 shows the development of torque strength over specified time intervals for inventive composition 1 as compared to Loctite Threadlocker 243. At all time intervals, inventive Composition 1 exhibited higher torque strength, and particularly at the 1 hour interval, where Composition 1 exhibited 10 nearly 50% greater torque strength than Loctite Threadlocker 243.

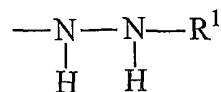
The examples set forth above serve to illustrate the present invention, but in no way are intended to limit the spirit and scope thereof, which is defined by the following claims.

**WHAT IS CLAIMED IS:**

1. An anaerobic adhesive composition, reaction products of which demonstrate improved initial room temperature torque strength on an oxidizable element, which element participates in curing said composition through its oxidation, said composition comprising:
  - 5 a.) at least one anaerobically curable (meth)acrylate monomer;
  - 10 b.) a cure system for said (meth)acrylate monomer comprising:
    - (i) at least one free radical generating material;
    - (ii) an acidic reducing agent for said free radical generating material, each of (i) and (ii) being present in substantially equal amounts;
    - 15 and
    - (iii) an accelerator for the reduction of said free radical generating material;
- 20 wherein said cure system is present in an amount sufficient to achieve about 30% or more of its 24 hour cured torque strength in about 5 minutes or less and wherein said anaerobic adhesive composition is free of maleic acid in the amount of 0.1 to 1% by weight of the total composition.
- 25 2. The composition of claim 1 wherein said free radical generating material is a peroxide compound.
- 30 3. The composition of claim 1 wherein said acidic reducing agent is saccharin.
4. The composition of claim 1 wherein said accelerator is a compound having the formula:

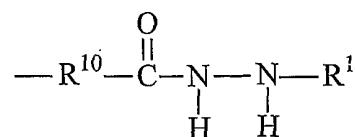


wherein R<sup>1</sup> is selected from the group consisting of alkyl from 2 to 6 carbon atoms, cycloalkyl, aryl, alkenyl and cycloalkenyl and R<sup>2</sup> is selected from the group consisting of hydrogen, alkyl, cycloalkyl, alkenyl, cycloalkenyl, aryl, alkoxy, aryloxy, carbonyl, amino, and the following groups:



5

and



wherein R<sup>10</sup> is selected from the group consisting of alkyl groups containing one to about 10 carbon atoms, alkenyl groups containing two to about 10 carbon atoms, and aryl groups containing up to about 10 carbon atoms.

5. The composition of claim 1 wherein said accelerator is selected from the group consisting of 1-acetyl-2-phenyl hydrazine, 1-acetyl-2(p-tolyl) para-toluene sulfonyl hydrazide, 1-formyl-2-phenyl hydrazine and combinations thereof.
- 10
6. The composition of claim 1 wherein said free radical generating source and said acidic reducing agent for said free radical generating material are each present in amounts of about 0.1% to about 10% by weight of the total composition.
- 15
7. The composition of claim 1 wherein each of (i) and (ii) of said cure system are present in about 1% by weight of the total composition.
- 20
8. The composition of claim 1 wherein said accelerator is present in amounts of about half of components (i) or (ii).
- 25

9. The composition of claim 1 wherein the initial room temperature torque strength is greater than about 50% of its fully cured strength in about 60 minutes or less.
- 5 10. The composition of claim 1 further including a component selected from the group consisting of stabilizers, sequestering agents, dyes, fluorescent agents, viscosity modifiers, accelerators and combinations thereof.
- 10 11. An anaerobic adhesive composition, reaction products of which demonstrate improved initial room temperature torque strength on an oxidizable element, which element participates in curing said composition through its oxidation, said composition comprising:
  - a.) at least one anaerobically curable (meth)acrylate monomer;
  - 15 b.) a cure system for said (meth)acrylate monomer consisting essentially of:
    - (i) at least one free radical generating material;
    - (ii) an acidic reducing agent for said free radical generating material, each of (i) and (ii) being present in substantially equal amounts; and
    - 20 (iii) an accelerator for the reduction of said free radical generating material;
- 25 wherein said cure system is present in an amount sufficient to achieve about 30% or more of its 24 hour cured torque strength in about 5 minutes or less and wherein said anaerobic adhesive composition is free of maleic acid in the amount of 0.1 to 1% by weight of the total composition.

12. An anaerobic adhesive composition, reaction products of which demonstrate improved initial room temperature torque strength on an oxidizable element, which element participates in curing said composition through its oxidation, 5 said composition comprising:

a.) at least one anaerobically curable alkyl (meth)acrylate monomer present in amounts of less than 60% by weight of the total composition;

10 b.) a cure system for said (meth)acrylate monomer comprising:

- (i) at least one free radical generating material;
- (ii) an acidic reducing agent for said free radical generating material, each of (i) and (ii) being present in substantially 15 equal amounts; and
- (iii) an accelerator for the reduction of said free radical generating material;

20 wherein said cure system is present in an amount sufficient to achieve about 30% or more of its 24 hour cured torque strength in about 5 minutes or less.

13. A method of preparing an anaerobic adhesive composition which reaches an initial room temperature torque strength on an oxidizable element, which 25 oxidizable element participates in curing through its oxidation, of about 30% or more of its 24 hour cured strength in about 5 minutes or less, said method comprising the steps of combining in admixture:

- (i) at least one anaerobically curable (meth)acrylate monomer;
- (ii) at least one free radical generating material;
- (iii) an acidic reducing agent for said free radical generating material, each of (i) and (ii) being present in substantially 30 equal amounts; and

(iv) an accelerator for the reduction of said free radical generating source;

5 wherein said anaerobic adhesive composition is free of maleic acid in the amount of 0.1 to 1.0% by weight of the total composition.

14. A method of bonding substrates comprising:

10 apply an anaerobic adhesive composition between mating parts capable of participating in anaerobic cure through their oxidation, said composition comprising:

15 (i) at least one free radical generating material;  
(ii) an acidic reducing agent for said free radical generating material, each of (i) and (ii) being present in substantially equal amounts; and  
(iii) an accelerator for the reduction of said free radical generating material; and

20 a.) permitting said anaerobic adhesive composition to cure,

25 wherein said cure system is present in an amount sufficient to achieve about 30% or more of its 24 hour cured torque strength in about 5 minutes or less and wherein said anaerobic adhesive composition is free of maleic acid in the amount of 0.1 to 1% by weight of the total composition.

15. A method of optimizing an adhesive composition to produce a set of desired physical properties comprising:

5           a.) providing in a machine readable storage medium a data set of adhesive composition components;

              b.) generating a statistically validated experimental design model comprising a set of adhesive compositions representing independent variables;

10           c.) generating objective test data of said set of adhesive composition from step b.), said test data results representing a set of dependent variables; and

              b.) establishing a correlation between said independent and dependent variables, whereby an optimized adhesive composition for the physical properties desired is generated.

15

16. The method of claim 15 wherein said statistical validation of said independent variable data sets is performed using statistical analysis.

20

17. The method of claim 15 wherein said objective test data includes data selected from the group consisting of physical strength data, stability data, heat-resistance data, cure speed data, viscosity data, solvent resistance data, cure through gap data, thermal expansion data, toughness data, solubility data, density data, modulus data, Tg data, heat aging data, and combinations thereof.

25

18. The method of claim 16 wherein said strength data includes data selected from the group consisting of torque data, tensile data, shear data, compression data, elongation data, impact data and combinations thereof.

30

19. The method of claim 15 wherein said correlation between the objective test data and the statistically validated data set is performed by using a neural network.

20. The method of claim 15 wherein said adhesive composition is selected from the group consisting of anaerobics, cyanoacrylates, silicones, epoxies, acrylics, and combinations thereof.

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 00/34681

A. CLASSIFICATION OF SUBJECT MATTER  
 IPC 7 C09J4/02 G06F17/50

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)  
 IPC 7 C09J G06F

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 practical, search terms used)

EPO-Internal, WPI Data, PAJ, CHEM ABS Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 321 349 A (RICH RICHARD D) 23 March 1982 (1982-03-23) cited in the application claims 1,6,7 ---	1-14
X	US 4 510 270 A (MORI HISAKAZU ET AL) 9 April 1985 (1985-04-09) column 3, line 25-29; table 4 ---	1-14
X	US 5 109 036 A (CHARRIERE BRUNO) 28 April 1992 (1992-04-28) claims 1,4,5; example 4 ---	1-14
X	US 5 126 416 A (YANG DARCHUN B) 30 June 1992 (1992-06-30) column 5, line 57 - line 63; claims 1,4,5,10; table I ---	1-14 -/-

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

## \* Special categories of cited documents :

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*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)
- \*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

\*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

\*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

\*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.

\*&\* document member of the same patent family

Date of the actual completion of the international search

12 June 2001

Date of mailing of the international search report

28/06/01

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## INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 00/34681

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 499 483 A (THREE BOND CO LTD) 19 August 1992 (1992-08-19) claim 2; examples 3,6 ---	1-14
T	WO 00 51045 A (STEWART LISA E) 31 August 2000 (2000-08-31) the whole document ---	15-20
A	MCEWAN W: "Taguchi methods and expert systems in fabrication design" INTERNATIONAL JOURNAL OF PRESSURE VESSELS AND PIPING, GB, ELSEVIER SCIENCE PUBLISHERS, BARKING,, vol. 53, no. 1, 1993, pages 47-61, XP002136605 ISSN: 0308-0161 the whole document -----	15-20

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US 00/34681

### Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1.  Claims Nos.: because they relate to subject matter not required to be searched by this Authority, namely:
  
2.  Claims Nos.: because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
  
3.  Claims Nos.: because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

### Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this International application, as follows:

see additional sheet

1.  As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
  
2.  As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
  
3.  As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
  
4.  No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

#### Remark on Protest

The additional search fees were accompanied by the applicant's protest.

No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International Application No. PCT/US 00 34681

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. Claims: 1-14

Anaerobic adhesive composition based on acrylate monomer, method for preparing said composition and method of bonding substrates by using said composition.

2. Claims: 15-20

Method for optimizing any adhesive composition

**INTERNATIONAL SEARCH REPORT**  
Information on patent family members

International Application No  
PCT/US 00/34681

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
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