

Description

This invention is directed to the repair of the integrity and/or surface imperfections of fiberglass, sheet metal or plastic structures which are defective because of accidental damage or flaws during the course of manufacture or subsequent use and handling.

It has been known in the art to patch damaged metal and/or fiberglass reinforced polyester objects with fiberglass cloth which has been saturated with either epoxy or polyester/styrene resin compositions. The resulting composites have many disadvantages such that they generally require that the resins be supplied as two separate components which must be premixed just prior to use. After the mixing has been completed the fiberglass cloth must be saturated with the premixed resin and applied rapidly to prevent premature gelation.

The time frame necessary for cure of such epoxys resins is generally measured in hours and/or over night. When they have finally cured, the cured composites have relatively poor resistance to impact forces since the cured epoxy and polyester/styrene resins are brittle materials that when impacted can produce severe cracking or total failure.

Epoxies, additionally, require an accurate mix ratio of resin and hardeners and a thorough mixing of both for uniform curing. Polyester/styrene compositions require that a small amount of hardener be mixed thoroughly with the resin, typical ratios being about 5:100 respectively. This provides potential operator errors leading to poor performance of repaired structures.

Laminate patches are well known. For example, US-A-3,189,509 discloses an Imperforate aluminum beaded sheet utilising an epoxy resin that is initially fluid to fill the interstices in a discontinuity of a damaged metal panel as well as the space between the beads on the aluminum sheet. A method of repairing discontinuities in fiberglass structures and utilizing either a polyester resin or the inventor's preferred variety of self-curing epoxy resins is clearly shown in US-A-3,814,645. A laminate patch for interiors which makes use of aluminum sheeting, paper layers and an overlay of plaster is shown in US-A-4,135,017. A method for repairing plastic materials in which a backing material is utilised to define a specific void behind the damage and then filling the discontinuity is covered in US-A-3,920,497. The use of repair patches in automotive tyres that utilise a first and second series of strips interwoven at right angles to one another and wherein the strips include reinforcing cords and uncured curable elastomers is shown in US-A-3,730,247.

The present invention overcomes many of the foregoing problems in repairing damage to the integrity of hollow structures. The present invention also provides a relatively simple means for repairing such structures while maintaining the structure in substantially its original geometry as well as restoring if not improving substantially all of the desirable physical properties to the damaged area.

According to the present invention, a method of repairing a workpiece comprises applying to the workpiece a porous, flexible, fibrous substrate impregnated with an adhesive for bonding the substrate to the workpiece, wherein the adhesive is acrylate-based and comprises a sulphur-bearing composition selected from chlorosulphonated polyethylene and a mixture of sulphonyl chloride with chlorinated polyethylene, and curing the adhesive by applying an activator, by brushing or spraying, to the surface of the impregnated substrate after applying the substrate, wherein the cured adhesive in the resultant patch has an impact strength of 0.32 to 1.6 J/mm (6 to 30 ft.lb/in).

It is preferred that the adhesive is formulated in such a manner that it is relatively stable under storage but such that it will, upon contact with the activator, react quickly to form the desired final cure. Some accelerating and/or activating components may be present in the adhesive provided other components necessary for activation are present in the separate activator such that curing of the adhesive is initiated only upon contact of the separate activator with the adhesive. It is particularly preferred that the separate activator should include, as an accelerator or curing activating ingredient, a condensation product of an aliphatic aldehyde with an aliphatic or aromatic amine and/or a material such as copper naphthenate.

The substrate is preferably porous and the adhesive composition can be calendered into it. The adhesive composition preferably consists essentially of a solution having a Brookfield viscosity of up to about 1 million and the sulphur-bearing composition contains about 25-70 wt.% of chlorine and about 3-150 mmoles sulphonyl chloride moiety per 100 g of polymer and being made from polyethylene having a melt index of about 4-500.

Particularly preferred adhesive compositions are compositions as described in EP-A-0142923 (Application No. 84306485.8) and comprise an acrylate (including methacrylate)-based ester monomer, a catalyst, a chlorinated or chlorosulphonated polyethylene polymer and a graft copolymer resin. Other modified methacrylate compositions are described in US-A-3,890,407 and US-A-4,182,644.

The adhesive may comprise an acrylate-based or methacrylate-based acid monomer, an acrylate-based or methacrylate-based ester monomer and chlorinated or chlorosulphonated polyethylene polymer resin and the graft copolymer resin for providing the composition with substantially enhanced overall adhesive physical properties. Catalyst will be provided either in the adhesive or separately, as discussed above.

The present invention utilises a flexible substrate such as fibreglass, artificial organic fibre materials compatible with acrylic adhesives (e.g. aramid fibre cloth, etc), graphite fibre cloth or metallic fibre structures.

Substrates such as these may have applied to them modified methacrylate-based resin compositions which impart the following advantages:

1. The resin and activator do not need to be mixed to effect a cure. The fibreglass cloth can be pre-impregnated with the resin and the activator sprayed on the impregnated cloth when hardening is desired.
2. The cured repair composites are much "tougher" or resistant to impact than the epoxy or polyester/styrene based materials, because the methacrylate-based compositions on which they are based have superior impact properties.
3. The modified methacrylate compositions adhere to a wider variety of materials, including most thermoplastic and thermoset engineering plastics, unprepared metals, painted metals, and oil or water contaminated surfaces. For example, they will generally fix anything that can be bonded such as steel, aluminum, PVC, ABS, acrylic, blends thereof, polycarbonates, other unprepared metals as well as the oil or water contaminated surfaces. Unfortunately they will not handle those other well known, tough to bond substrates such as polyethylene, polypropylene, fluorocarbon plastics, or vulcanized rubber.

While many modified methacrylate adhesive compositions can be used as saturating resins for the composites of the instant invention, the most useful are those which combine the advantages of:

1. fast curing;
2. no-mix or simple 1:1 equal volume mix;
3. high impact strength; and
4. good adhesion to a wide variety of materials including unprepared metals, painted metals, plastics and moist or oil contaminated surfaces.

These requirements are generally met by the preferred and most preferred compositions referred to above. The impact strength of the cured adhesive compositions used to saturate the fibreglass substrate contributes directly to the impact strength of the composite repair. The impact strength of the adhesive composite can be measured as described in EP-A-0142923.

It should be noted that certain other modified acrylic compositions may prove to be useful in the instant invention are described in US-A-3,333,025; US-A-3,725,504; US-A-3,970,709 and US-A-4,293,665. These do have a deficiency, however, in that they generally perform best when premixed in hardener to resin ratios of about 2-6:100. Another class of modified methacrylate adhesive which could be used as saturating resins for the instant invention is disclosed in US-A-4,308,503.

In general, the impact strength of epoxy-based compositions with relatively rapid cure rates at room temperature is less than 0.27 J/mm (5 ft.lbs. per sq. inch). The impact strength of the polyester/styrene compositions is generally lower than that of the epoxies, i.e. less than 0.16 J/mm (3 ft. lbs. per sq. inch). On the other hand, the impact strength of the preferred methacrylate-based compositions as described in US-A-3,890,407 and US-A-4,182,644 fall in the range of from 0.43 to 0.8 J/mm (8 to 15 ft. lbs. per sq. inch).

It is generally important that these composites be impact resistant in the temperature range of normally anticipated use, that is, from -31 °C to +65 °C (-20 °F to +150 °F). However, if particular service conditions are anticipated which require enhancement of a given property such as heat, chemical or moisture resistance, impact strength under normal conditions might be compromised. Specifically, if a high impact strength is required at an operating temperature of +71 °C (+200 °F), it is possible that the saturating resin capable of operating in that temperature range will have a reduced impact strength on the order of 0.27 J/mm (5ft.lbs. per sq. inch) at room temperature.

Unless otherwise indicated in the following examples, two types of fibreglass supporting cloth were used. Their physical descriptions are as follows:

	Fiberglass Tape	Fiberglass Cloth
Style	#2964 woven edge	CD8 340
Width	2 inch (50.8mm)	Variable
Thickness	.012 inch (.30mm)	.047 inch (1.2mm)
Weave	Plain	Triaxial
Weight	28.8 g/m ² (8.5 oz/yd ²)	115 g/m ² (34 oz/yd ²)
Count	17x18	not specified
Supplier	Mutual Industries Red Hill, PA.	Nytex Corp.

TABLE I

ADHESIVE		ACTIVATOR	
Ingredients	Weight Percent	Ingredients	Weight Percent
Hypalon® 48S CSPE ¹	18.14	VYNS ⁵ resin	4.76
Methyl methacrylate	57.60	Methyl ethyl ketone	71.41
Methacrylic acid	5.90	Vanax® 808 ⁶	23.80
Ethylene glycol dimethacrylate	1.36	Copper Naphthenate Solution	0.024
Cumene hydroperoxide	.45		
Ionol® ²	0.23		
Milled glass fibers ³	13.60		
Fumed silica ⁴	2.72		

Footnotes:

1. CSPE = Chlorosulfonated polyethylene
2. Shell Chemical Company brand of 2, 6-di-t-butyl-4-methylphenol
3. Grade 731 B/A, 0.8 mm (1/32 inch) length, Owens-Corning Fiberglas
4. Cab-O-Sil brand, Grade M-5 Cabot Corp.
5. Vinyl Chloride/Vinyl Acetate Copolymer, Union Carbide Corp.
6. Butyraldehyde-Aniline condensation product, R.T. Vanderbilt Company
7. 8 percent copper, Tenneco Chemicals, Inc.

The adhesive resin of Table I was prepared in a 208 litre (55 gallon) steel drum using a ten horsepower "Hockmeyer" high-speed disperser. The total batch weight was 340 lb. (154kg) with the percentage of each ingredient present in the amount indicated in Table I.

The Hypalon® 48S chlorosulfonated polyethylene and methyl methacrylate monomer were mixed until all of the "Hypalon®" was dissolved or dispersed (approximately three hours). The remaining ingredients were added and the mixture stirred for an additional forty-five minutes.

The adhesive activator of Table I was prepared by rolling the ingredients in a glass jar on a jar mill until all components were dissolved.

EXAMPLE I

The adhesive resin of Table I was applied to 3 in (7.5cm) lengths of the fiberglass tape described above at a coverage rate approximately 0.07 oz. per inch (0.8 gm per cm).

The damaged corner of a fiberglass reinforced polyester tray dimensions of 19 in. length x 12.5 in width x 6 in depth (48.25 cm x 31.75 cm x 15.25 cm) was brushed with a liberal coat of the activator solution of Table I. Three lengths of the resin-impregnated cloth were applied in an overlapping fashion and successively brushed with activator solution such that the damaged area was completely covered.

The patched area was tack-free within ten minutes and then hardened rapidly with the evolution of heat during the next five minutes. After 30 minutes the repaired area was impacted repeatedly with a 12 oz. (340 gram) hammer. The hardened patch was substantially undamaged, while the fiberglass tray fractured in the area surrounding the patch.

EXAMPLE II

Thirty-six inches (91cm) of fiberglass tape was aligned lengthwise and centered upon a 40 in. (102 cm) length of .004 in (0.1 mm) thick polyethylene film. The adhesive solution of Table I was poured along the center of the entire length of the fiberglass tape and spread evenly to cover the tape completely. The tape was inverted on the polyethylene film and the coating process repeated. The average weight of resin per unit length of tape was 0.67 oz/in (0.75 gm/cm).

The ends of the polyethylene film were folded over the ends of the coated fiberglass tape. Similarly, the protruding edges of the polyethylene film were folded toward the center of the fiberglass tape along its entire length to completely enclose it. The protected tape was then rolled up with the folded seam inside and placed in a 11.3 g (four ounce) wide-mouth jar for storage and later use.

The tape described above and the adhesive activator of Table I were used to make a simulated repair on a four inch (10.2 cm) length of 0.75 inch (1.90 cm) Schedule 80 polyvinyl chloride (PVC) pipe. The pipe section was threaded on each end so that fittings could be applied to enable hydrostatic burst testing of the repaired pipe section.

Two holes 0.125 in (3.18 mm) in diameter were drilled near the center of a pipe section 180° apart on the circumference of the pipe. The pipe was then lightly sanded and wiped clean with methyl ethyl ketone, in the area of the repair. The pipe was then coated with the activator solution of Table I over a sufficient area to totally contact and activate the adhesive resin on the bandage. The activator was applied from a 2.8 g (one ounce) narrow-mouth laboratory bottle fitted with a small pneumatic pump spraying device.

A 3 inch (7.6 cm) length of the coated fiberglass tape described above wrapped circumferentially about the pipe, centered over the two holes. Before overlapping the first layer of the tape, the outside of the applied tape was sprayed with activator solution. The remaining tape was wrapped around the pipe and the entire repair was sprayed again with activator solution. The completed repair was such that one hole was covered with one layer of tape, the second with two.

The repair was tack-free in about ten minutes and hard to the touch in fifteen minutes. The repaired pipe was allowed to stand for twenty-four hours at 70° F (22° C) before testing.

The burst tests were performed by fitting one end of the repaired pipe section with a threaded cap of corresponding size and schedule. The other end was attached via a metal fitting to a hydraulic ram pump fitted with a pressure indicating dial gauge. The pipe section and hydraulic system of the pump were filled with hydraulic oil and all air was bled from the system prior to the burst test. All fittings were then secured, and the pump was activated to increase the ram pressure until failure was indicated by oil leakage and a drop in the indicated ram pressure. This test is an adaptation of ASTM method 1599-69.

When pressure tested according to the above described method, the repaired area began to leak from the area of the hole with a single overlap of tape at an indicated dial pressure of 2500 lb/sq in (176 Kg/sq cm). An unperforated control test pipe failed by fracture at an indicated dial pressure of 2600 lb/sq in (18.3 Kg/sq cm).

EXAMPLE III

example II was repeated, except that 0.75 in (1.9 cm) black iron pipe was used in place of PVC pipe.

The pipe was prepared by wiping it with methyl ethyl ketone, sanding it with 60 grit sandpaper, and wiping with methyl ethyl ketone again. The repair was done as in Example II.

When pressure was applied, the repaired area started to leak at an indicated dial pressure of 900 lb/in (6.3 Kg/cm).

EXAMPLE IIIA

Example III was repeated except that a longer piece of fiberglass was used to go around the pipe 2.5 times covering each hole with two layers.

When pressure was applied, the repaired area did not start to leak until the indicated dial pressure of 2600 lb/in (18 Kg/cm).

TABLE II

ADHESIVE		ACTIVATOR	
Ingredients	Weight Percentage	Ingredients	Weight Percentage
40% Hypalon® 30 in MM ¹ monomer	44.40	VYNS ³ resin	4.76
		Methyl ethyl ketone	71.34
25% Acryloid KM-452 in MMA ¹ monomer	44.40	Vanax® 808 ⁴	23.78
Methacrylic Acid	8.87	Copper Naphthenate Solution ⁵	0.12
Ethylene glycol dimethacrylate	1.77		
Cumene hydroperoxide	.44		
Ionol® ²	.22		

Footnotes:

1. MMA = methyl methacrylate

2. Shell Chemical Company brand of 2, 6-di-t-butyl-4-methylphenol

3. Vinyl Chlorid-vinyl acetate copolymer, Union Carbide

4. Butyraldehyde-aniline condensation product, R.T. Vanderbilt Company

5. Eight percent copper, Tenneco Chemicals, Inc.

The adhesive solution of Table II was prepared from separate master-batches of Hypalon® 30 chlorosulfonated polyethylene and Acryloid® KM-452 methacrylate-acrylonitrile-butadiene-styrene (MABS) resin in methyl methacrylate monomer. The masterbatch of Hypalon® was prepared by rolling the polymer and monomer in a glass jar on a jar mill until the polymer was completely dispersed or dissolved in the monomer. The KM-452 solution masterbatch was prepared by mixing the polymer and monomer in a four quart (3.8 liter) laboratory "Hobart" mixer for 90 minutes.

The masterbatches were combined in the indicated proportions with the remaining ingredients and mixed thoroughly by hand until uniform.

The adhesive activator of Table II was prepared according to the method of Table I.

EXAMPLE IV

A 10 inch x 10 inch (25.4 cm x 25.4 cm) square of the triaxial cloth described above was placed on one or more sheets of aluminum foil of sufficient area to completely wrap or seal the cloth to prevent the monomers in the adhesive resin from evaporating and to permit its use at a later stage. The adhesive resin of Table II was spread evenly over both sides of the fiberglass cloth as described in Example II, except that the coverage rate was increased to 0.63 oz/sq in (0.3 gm/sq cm) to saturate the thicker cloth. The aluminum foil was folded over the coated cloth and the package was allowed to stand overnight at 70° C to allow the adhesive resin to fully impregnate the interstices of the cloth.

A 16 in x 16 in x .062 in (381 mm x 381 mm x 1.57 mm) sheet of aluminum with a three inch (7.62 cm) hole in the center was used to demonstrate the repair of damaged sheet metal structures. The repair was made as described below without cleaning or abrading the surface of the aluminum.

The aluminum foil package was placed on a table with the folded seams upward and then opened to expose the resin-impregnated patch. The entire surface of the patch was sprayed with a liberal coat of the activator solution of Table II, using the device described in Example II. With the aluminum foil still in place, the activated side of the patch was placed over and centered about the hole in the aluminum sheet and smoothed over the surrounding metal. The aluminum foil was then peeled from the patch and adhesive on the patch was smoothed with a wooden stick, paying particular attention at the edges. The entire patch was then sprayed with activator solution. The patch was tack-free in five minutes. The area of the patch over the hole (with no metal contacting to remove the heat of chemical reaction) hardened with the evolution of considerable heat within five to eight minutes. The area of the patch in contact with the metal hardened in 9-12 minutes with less evidence of heat of chemical reaction due to the dissipating effect of the metal.

Fifteen minutes after the application was completed, the center of the patch was impacted repeatedly with a 12 oz. (340 gm) ball-peen hammer without cracking or otherwise damaging the patch. Similar impacting of the surrounding aluminum caused significant dimpling and distortion of the panel, indicating that the repair patch had significantly more resistance to structural damage by impact than the panel itself.

EXAMPLE V

A 3.5 in x 4 in x .010 in (88.9mm x 101.6 mm x 0.25 mm) piece of Kevlar®, aramid fiber cloth (17 x 17 count) was coated with 10g of the adhesive solution of Table II in the manner used in the above examples.

The coated patch was sprayed with the activator solution of Table II and placed on an intact sheet of aluminum similar to that of Example IV. The patch was then sprayed with activator. The patch was tack-free within five minutes and hard to the touch in ten minutes.

1. Registered trademark of E.I. du Pont.

EXAMPLE VI

Example VI was repeated using a similar size piece of (13 x 13 count) graphite fiber cloth. The patch was tack-free in six minutes and hard to the touch in 15 minutes.

EXAMPLES VII-IX

In the following examples, commercially available methacrylate-based adhesives were used to impregnate three inch lengths of fiberglass tape. The coated patches of tape were activated and applied to aluminum sheets in the manner of examples V and VI, with the results noted below:

Example	Adhesive	Activator	Tack-Free Time (min.)	Hardening Time (min.)
VII	"Dymax" 828	"Dymax" 530	4.5	5-10
VIII	"Dymax" 828	Table II	3-4	4-6
IX	"Versilok" 201	"Versilok" No.4	8-9	120

Footnotes:

1. "Dymax" is a trademark of the American Chemical and Engineering Company.
2. Contains aldehyde-amine reaction product.
3. Diluted with two volumes of methyl ethyl ketone to facilitate application.
4. Versilok is a trademark of the Chemical Products Division of the Lord Corporation.

EXAMPLE X

Starting with a square of triaxial fiberglass cloth of either a 25.4 mm (12 inch) square or a 19 mm (9 inch) square having a Reemay® layer or veil face is placed face down within a square package of foil. The resin from Table II is applied in a uniform film thickness over the entire top surface. The acrylic adhesive was calendered onto the surface with a suitable straight-edge or blade. After the resin had been applied it was transferred to the piece of heat sealable aluminum foil packaging material keeping the dry Reemay® side down. The package was then closed with a second piece of foil sheet with a slight pressure being applied over the top piece of foil to alleviate air pockets. Heat sealing of the foil was accomplished with well known heat sealing equipment.

This sealed patch was brought to the situs of a damaged aluminum shipping container. Grease, grime and loose dirt in the patching area were briefly wiped away. The sealed foil package was opened and one side of the patch area was sprayed with the activator from Table II. The impregnated patch pressed into place with the back of the foil package. Moderate pressure was applied to the patch with a wooden roller. The top of the patch was sprayed with the activator from Table II. The patch was tack free within 5 minutes and totally hard within 15 minutes.

1. Reemay® is a trademark of du Pont for its spunbonded polyester cloth.

EXAMPLE XI

The procedure set forth in Example X was followed with the same materials, however, within 30 seconds of the final spray application of activator catalyst on the exterior surface a thin sheet of malleable aluminum was applied, in order to provide additional cosmetic effect to the exterior of the aluminum container on which the patch was placed. The thickness of this aluminum sheet was on the order of 62 to 125 µm (.0025 to .0050 inches).

The preferred patch for use with large shipping containers, be they of fiberglass or metal skin construction, is of the triaxial fiberglass fabric impregnated with the resin. This triaxial fabric maximizes puncture and impact resistance.

The compositions set forth offer the advantages that they are usable at room temperature, no heat being required either for applying the compositions to the substrates or curing. They can be used on porous surfaces and those having bonds containing elastomeric polymers such as chlorosulfonated polyethylene are flexible. The instant compositions do not require a careful surface preparation but can be used, for example on bonderized or oily steel, aluminum, other metals, polar polymeric materials (i.e., those having various functional groups, e.g. polyesters, polyamides, polyurethanes, polyvinyl chloride, etc.), wood, pre-painted surfaces, glass and paper.

While the invention has been illustrated by certain examples of preferred and greatly preferred embodiments thereof, all parts, proportions and percentages have been by weight unless otherwise indicated.

Claims

1. A method for repairing a workpiece, comprising applying to the workpiece a porous, flexible, fibrous substrate impregnated with an adhesive for bonding the substrate to the workpiece, wherein the adhesive is acrylate-based and comprises a sulphur-bearing composition selected from chlorosulphonated polyethylene and a mixture of sulphonyl chloride with chlorinated polyethylene, and curing the adhesive by applying an activator, by brushing or spraying, to the surface of the impregnated substrate after applying the substrate, wherein the cured adhesive in the resultant patch has an impact strength of 0.32 to 1.6 J/mm (6 to 30 ft.lb/in).
2. A method according to claim 1, wherein the flexible substrate is selected from a metallic fibre structures, fibreglass, graphite fibre cloth and artificial organic fibre materials compatible with acrylic acids.
3. A method according to claim 2, wherein the artificial organic fibre material is an aramid fibre cloth.
4. A method according to claim 2, wherein the substrate is a fibreglass fabric.
5. A method according to claim 4, wherein the substrate comprises at least three layers of fibreglass fibres and the fibres in each layer are aligned in parallel.
6. A method according to any preceding claim, wherein the substrate additionally includes a thin metallic panel conforming to the workpiece to be repaired.
7. A method according to any preceding claim, which additionally comprises applying the adhesive composition to the substrate as a solution having a Brookfield viscosity of up to about 1 million, and the sulphur-bearing composition contains about 25-70 wt.% of chlorine and about 3-150 mmoles sulphonyl chloride moiety per 100 g of polymer and being made from polyethylene having a melt index of about 4-500.
8. A method according to claim 7, wherein the sulphur-bearing composition is chlorosulphonated polyethylene, wherein the relative weight proportions of chlorosulphonated polyethylene and the monomer are 100:25-1000, respectively, and wherein the accelerator is a primary amine-aldehyde condensation product.
9. A method according to any of claims 1 to 8, wherein the adhesive comprises an acrylate-based or methacrylate-based ester.
10. A method according to claim 9, wherein the adhesive composition includes an acrylate-based or methacrylate-based acid monomer.
11. A method according to any preceding claim, wherein the adhesive is applied to the substrate which is then sealed in a foil package until just prior to its use on the workpiece, thereby preserving the adhesive in a liquid state until utilised.



The preferred patch for use with large shipping containers, be they of fiberglass or metal skin construction, is of the triaxial fiberglass fabric impregnated with the resin. This triaxial fabric maximizes puncture and impact resistance.

The compositions set forth offer the advantages that they are usable at room temperature, no heat being required either for applying the compositions to the substrates or curing. They can be used on porous surfaces and those having bonds containing elastomeric polymers such as chlorosulfonated polyethylene are flexible. The instant compositions do not require a careful surface preparation but can be used, for example on bonderized or oily steel, aluminum, other metals, polar polymeric materials (i.e., those having various functional groups, e.g. polyesters, polyamides, polyurethanes, polyvinyl chloride, etc.), wood, pre-painted surfaces, glass and paper.

While the invention has been illustrated by certain examples of preferred and greatly preferred embodiments thereof, all parts, proportions and percentages have been by weight unless otherwise indicated.

15 Claims

1. A method for repairing a workpiece, comprising applying to the workpiece a porous, flexible, fibrous substrate impregnated with an adhesive for bonding the substrate to the workpiece, wherein the adhesive is acrylate-based and comprises a sulphur-bearing composition selected from chlorosulphonated polyethylene and a mixture of sulphonyl chloride with chlorinated polyethylene, and curing the adhesive by applying an activator, by brushing or spraying, to the surface of the impregnated substrate after applying the substrate, wherein the cured adhesive in the resultant patch has an impact strength of 0.32 to 1.6 J/mm (6 to 30 ft.lb/in).
2. A method according to claim 1, wherein the flexible substrate is selected from a metallic fibre structures, fibreglass, graphite fibre cloth and artificial organic fibre materials compatible with acrylic acids.
3. A method according to claim 2, wherein the artificial organic fibre material is an aramid fibre cloth.
4. A method according to claim 2, wherein the substrate is a fibreglass fabric.
5. A method according to claim 4, wherein the substrate comprises at least three layers of fibreglass fibres and the fibres in each layer are aligned in parallel.
6. A method according to any preceding claim, wherein the substrate additionally includes a thin metallic panel conforming to the workpiece to be repaired.
7. A method according to any preceding claim, which additionally comprises applying the adhesive composition to the substrate as a solution having a Brookfield viscosity of up to about 1 million, and the sulphur-bearing composition contains about 25-70 wt.% of chlorine and about 3-150 mmoles sulphonyl chloride moiety per 100 g of polymer and being made from polyethylene having a melt index of about 4-500.
8. A method according to claim 7, wherein the sulphur-bearing composition is chlorosulphonated polyethylene, wherein the relative weight proportions of chlorosulphonated polyethylene and the monomer are 100:25-1000, respectively, and wherein the accelerator is a primary amine-aldehyde condensation product.
9. A method according to any of claims 1 to 8, wherein the adhesive comprises an acrylate-based or methacrylate-based ester.
10. A method according to claim 9, wherein the adhesive composition includes an acrylate-based or methacrylate-based acid monomer.
11. A method according to any preceding claim, wherein the adhesive is applied to the substrate which is then sealed in a foil package until just prior to its use on the workpiece, thereby preserving the adhesive in a liquid state until utilised.



12. A method according to any preceding claim, wherein the activator is applied by spraying.

Patentansprüche

- 5 1. Verfahren zum Reparieren eines Werkstücks, gekennzeichnet durch ein Anbringen eines porösen, flexiblen, faserigen Substrats am Werkstück, wobei das Substrat mit einem Klebstoff zum Verbinden des Substrats mit dem Werkstück durchtränkt wird, der Klebstoff auf Acrylatbasis ist und eine Schwefel enthaltende Verbindung einschließt, die aus chloresulfoniertem Polyethylen und einer Mischung von Sulfonylchlorid mit chloriertem Polyethylen ausgewählt ist, und durch ein Aushärten des Klebstoffs durch Auftragen eines Aktivators, durch Streichen oder Sprühen, auf die Oberfläche des getränkten Substrats nach Anbringen des Substrats, wobei der ausgehärtete Klebstoff in dem resultierenden Ausbesserungsstück eine Schlaghärte von 0,32 bis 1,6 J/mm (6 bis 30 ft.lb/in) hat.
- 10 2. Verfahren gemäß Anspruch 1, wobei das flexible Substrat aus metallischen Faserstrukturen, Fiberglas, Graphitfaserstoff und künstlichen organischen Fasermaterialien, die mit Acrylsäure kompatibel sind, ausgewählt ist.
- 15 3. Verfahren gemäß Anspruch 2, wobei das künstliche organische Fasermaterial ein Aramidfaserstoff ist.
- 20 4. Verfahren gemäß Anspruch 2, wobei das Substrat ein Fiberglasstoff ist.
5. Verfahren gemäß Anspruch 4, wobei das Substrat mindestens drei Schichten Fiberglasfasern enthält und die Fasern in jeder Schicht parallel angeordnet sind.
- 25 6. Verfahren gemäß einem der vorhergehenden Ansprüche, wobei das Substrat zusätzlich eine dünne Metallplatte enthält, die das zu reparierende Werkstück festigt.
- 30 7. Verfahren gemäß einem vorhergehenden Anspruch, das zusätzlich ein Auftragen der Klebstoffverbindung auf das Substrat als eine Lösung, die eine Brookfield-Viskosität von bis zu ungefähr 1 Mio hat, aufweist und bei der die Schwefel enthaltende Verbindung ungefähr 25 bis 70 Gew.-% Chlor und ungefähr 3 bis 150 mmol Sulfonylchloridanteil pro 100 g Polymer enthält und aus Polyethylen besteht, das einen Schmelzindex von ungefähr 4 bis 500 hat.
- 35 8. Verfahren gemäß Anspruch 7, wobei die Schwefel enthaltende Verbindung chloresulfoniertes Polyethylen ist, die relativen Gewichtsverhältnisse des chloresulfonierten Polyethylens und des Monomers 100:25 bis 1000 sind und der Beschleuniger ein primäres Aminoaldehydkondensationsprodukt ist.
- 40 9. Verfahren gemäß einem der Ansprüche 1 bis 8, wobei der Klebstoff einen Ester auf Acrylatbasis oder Methacrylatbasis enthält.
- 45 10. Verfahren gemäß Anspruch 9, wobei die Klebstoffverbindung ein Säuremonomer auf Acrylatbasis oder Methacrylatbasis enthält.
11. Verfahren gemäß einem vorhergehenden Anspruch, wobei der Klebstoff auf das Substrat aufgetragen wird, das danach in einer Folienverpackung abgedichtet wird bis kurz vor seiner Verwendung auf dem Werkstück, wodurch der Klebstoff in einem flüssigen Zustand bis zur Verwendung gehalten wird.
- 50 12. Verfahren gemäß einem vorhergehenden Anspruch, wobei der Aktivator durch Besprühen aufgetragen wird.

Revendications

- 55 1. Procédé pour réparer une pièce, comprenant l'application à la pièce d'un substrat fibreux, flexible, poreux, imprégné d'un adhésif pour lier le substrat à la pièce, l'adhésif étant un adhésif à base d'acrylate et comprenant une composition renfermant du soufre choisie entre un polyéthylène chlorosulfoné et un mélange de chlorure de sulfonyle avec un polyéthylène chloré, et le durcissement de l'adhésif en appliquant un activateur, par passage à la brosse ou pulvérisation, à la surface du substrat imprégné après application du substrat, l'adhésif durci dans la pièce résultante ayant une résistance au



choc de 0,32 à 1,6 J/mm (6 à 30 ft.lb/in).

2. Procédé suivant la revendication 1, dans lequel le substrat flexible est choisi entre une structure en fibres métalliques, la fibre de verre, une étoffe de fibres de graphite et des matières à base de fibres organiques synthétiques compatibles avec des acides acryliques.
3. Procédé suivant la revendication 2, dans lequel la matière à base de fibres organiques synthétiques est une étoffe de fibres d'aramide.
4. Procédé suivant la revendication 2, dans lequel le substrat est une étoffe de fibres de verre.
5. Procédé suivant la revendication 4, dans lequel le substrat comporte au moins trois couches de fibres de verre et les fibres dans chaque couche sont alignées parallèlement.
6. Procédé suivant l'une quelconque des revendications précédentes, dans lequel le substrat renferme en outre un panneau métallique mince renforçant la pièce à réparer.
7. Procédé suivant l'une quelconque des revendications précédentes, qui comprend en outre l'application de la composition d'adhésif au substrat sous forme d'une solution ayant une viscosité Brookfield allant jusqu'à environ 1 million, la composition renfermant du soufre contenant environ 25 à 70 % en poids de chlore et environ 3 à 150 mmoles de groupements chlorure de sulfonyle pour 100 g de polymère et étant constituée d'un polyéthylène ayant un indice de fluidité d'environ 4 à 500.
8. Procédé suivant la revendication 7, dans lequel la composition renfermant du soufre est un polyéthylène chlorosulfoné, le rapport pondéral du polyéthylène chlorosulfoné au monomère, respectivement, étant égal à 100:25-1000, et l'accélérateur est un produit de condensation amine primaire-aldéhyde.
9. Procédé suivant l'une quelconque des revendication 1 à 8, dans lequel l'adhésif comprend un ester à base d'un acrylate ou à base d'un méthacrylate.
10. Procédé suivant la revendication 9, dans lequel la composition d'adhésif renferme un monomère acide à base d'acrylate ou à base de méthacrylate.
11. Procédé suivant l'une quelconque des revendications précédentes, dans lequel l'adhésif est appliqué au substrat qui est ensuite logé hermétiquement dans un emballage constitué d'une feuille métallique jusqu'à un moment situé juste avant son utilisation sur la pièce, ce qui permet de conserver l'adhésif à l'état liquide jusqu'à son utilisation.
12. Procédé suivant l'une quelconque des revendications précédentes, dans lequel l'activateur est appliqué par pulvérisation.