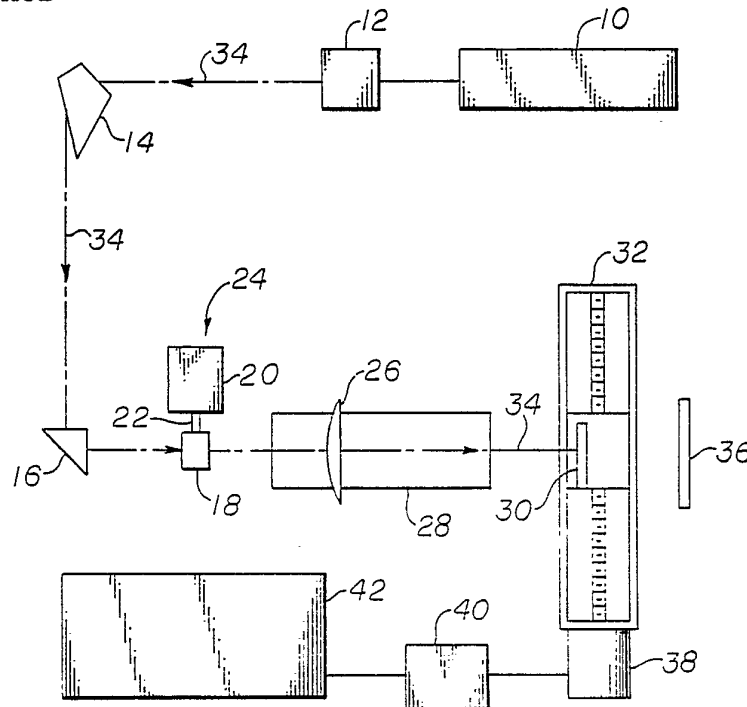




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<p>(21) International Application Number: PCT/US86/01328 (22) International Filing Date: 18 June 1986 (18.06.86) (31) Priority Application Number : 746,170 (32) Priority Date : 18 June 1985 (18.06.85) (33) Priority Country: US (71) Applicant: THE DOW CHEMICAL COMPANY [US/US]; 2030 Dow Center, Abbott Road, Midland, MI 48640 (US). (72) Inventors: VOLKMANN, Curtis, L. ; 1901 Eastlawn Drive, Apt. A-11, Midland, MI 48640 (US). KESTER, John, J. ; 5401 Nurmi, Midland, MI 48640 (US). STEVENS, Gregory, A. ; 5001 Oakridge Drive, Midland, MI 48640 (US).</p>		<p>(74) Agent: RUSSELL, H., David; The Dow Chemical Company, P.O. Box 1967, Midland, MI 48641-1967 (US). (81) Designated States: AU, BR, DE (European patent), FR (European patent), GB (European patent), IT (European patent), JP, KR, NL (European patent), SE (European patent). Published <i>With international search report.</i></p>

(54) Title: METHOD FOR PRODUCING ENHANCED BONDS BETWEEN SURFACES AND ARTICLES PRODUCED BY THE METHOD



(57) Abstract

A method for making an article containing and adhesively bonded joint by first placing the surfaces (30) to be bonded in the path of an intense energy beam (34), such as a laser beam, for a short duration to modify the surfaces (30). Then an adhesive is applied to the modified surfaces (30) and the joint is completed. The inventive method results in stronger and more durable bonds relative to untreated surfaces (30) and relative to prior surface treatments such as solvent cleaning. An article made using the above method.

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METHOD FOR PRODUCING ENHANCED BONDS BETWEEN
SURFACES AND ARTICLES PRODUCED BY THE METHOD

The present invention relates to a method for making an improved adhesive bond.

A need has long existed for a method of enhancing the adhesive bonding characteristics of various materials. This need has extended to enhancing the bonding characteristics of materials which are essentially clean surfaces, e.g., solvent cleaned surfaces, as well as enhancing the bonding characteristics of contaminated surfaces, e.g., surfaces covered with a protective coating such as a wax or oil coated surface. These needs have developed for example out of the automotive and aircraft industries' dissatisfaction with current surface treatment techniques and bonding results.

An elegant explanation of material treatment using energy beams comprising laser beams is contained in U. S. Patent 4,122,240 granted to Banas et al. Figure 1 therein shows a plot of absorbed power density versus interaction time. At relatively low absorbed power density applied for relatively long times, materials can be heated to appreciable depths without melting the surface and thus can be subjected to "transformation hardening." At very high absorbed power density applied for extremely short periods of time to a surface coated with a thin layer of preferably black paint (which enhances absorption of the laser beam) surface vaporization of the paint is so violent that a shock wave of sufficient amplitude moves through the material that can result in "shock hardening" (see U. S. Patent 4,401,477 to Clauer et al.). At mid-absorbed power density applied for intermediate time periods, the irradiated material can be vaporized to a significant depth for "hole drilling" applications. At lower power density applied for longer time periods, the material can be melted to significant depths for "deep penetration welding." Using approximately the same absorbed power density as in "deep penetration welding," but for shorter periods of time, Banas et al. achieved "skin melting." In skin melting a thin layer of the material irradiated is melted but not vaporized and then rapidly self-cooled.

Langen et al. in U. S. Patent 4,368,080 apply 0.5 to 16 joules/cm² per pulse and a pulse time of from 1 to 100 microseconds to clean rust from metallic objects prior to painting. The power density used by Langen et al. is relatively low to prevent melting or vaporization of the parent metal, but high enough to

vaporize the rust or to convert the rust to a form not detrimental to subsequent paint performance.

In Japanese Patent Application 54-26509 of Iuchi et al. a laser is used to remove oil from steel plates prior to painting. The oil is compounded with light absorbing chemicals to improve the efficiency of conversion of the light energy into heating the oil film and only the oil is vaporized, not the underlying steel. In Japanese Patent 81,116,867 zinc galvanized steel sheets are polished to remove the zinc coating, irradiated with a laser beam to remove residual zinc, phosphate treated and then painted.

Patent No. 211,801 from the German Democratic Republic claims a process for the modification of surface properties of semi-finished products and molded materials made of olefin copolymers. Examples of the process use ionizing radiation, such as corona discharge and energy beams from an electron accelerator, to heat the surface to a temperature between 340 and 410°K. Other forms of ionizing radiation are suggested without examples, such as ultraviolet, x-ray, gamma or laser radiation and particle radiation such as alpha or beta radiation. Improvement of the adhesiveness, printability, metallizability and varnishability is taught in this patent.

The present invention is a new utility for surfaces modified by an energy beam, e.g., a laser beam. This new utility is enhanced bonding characteristics using an adhesive to bond together at least two surfaces, enhanced relative to a comparable

untreated surface or surfaces. In many cases, enhanced bonding characteristics are also shown to be achieved relative to a comparable solvent washed surface or surfaces. The term "enhanced bonding characteristics" refers to a bond having at least one of the following enhanced properties: at least a 20 percent stronger bond as demonstrated by a standard lap shear test; a more durable bond upon exposure to a sodium chloride solution/high humidity environment as demonstrated using the durability/lap shear test of Example 4; a more durable bond upon exposure to moisture as demonstrated by at least a 25 percent shorter crack extension in a modified standard crack extension wedge test; a stronger bond as demonstrated by at least a 25 percent shorter initial crack in a modified standard wedge test; at least a 25 percent longer time of immersion in a boiling water bath before debonding in the test of Example 29; at least a 20 percent higher pull strength as demonstrated by the ASTM 1876-72 peet test; at least a 20 percent higher impact strength as demonstrated by a modified ASTM D-256-81 impact test; at least a 20 percent higher torque strength using the torque test of Example 30; or at least a 25 percent reduction in the area of bond failure at the interface between the adhesive and the bonded surface in any of the tests above with a commensurate increase in failure within the adhesive itself or in the bonded material.

Prior techniques for enhancing the bonding characteristics of materials include sandblasting, shot peening, brushing, pickling with acid, anodizing and washing with solvents, see for example, "Adhesives Technology Handbook," A. H. Landrock, 1985, Noyes

Publications, ISBN 0-8155-1040-3. All of these techniques have undesirable features such as waste disposal of spent chemicals. Nevertheless, surface treatment usually results in enhanced bondability. For example, 5 galvanized steel sheets formed into automotive door panels are generally coated with a lubricant prior to forming to extend forming die life and to preserve the surface finish of the panel. However, before the panel can be fastened to other parts with an adhesive, the 10 lubricant usually needs to be removed from the panel, e.g., by washing with a solvent, for yet improved bondability. Often, even better bondability can be obtained by additionally roughening or etching the panel surface to be bonded by sandblasting and/or 15 chemical treatment, such as a phosphate treatment. The present invention cleans the surface of a material and can also be used to vaporize or melt the material itself or otherwise modify the surface, said modified surface especially suitable for adhesion purposes.

20 Terms

The term "magnesium-containing material" means (1) magnesium or (2) alloys having magnesium as the predominant component.

The term "aluminum-containing material" means 25 (1) aluminum or (2) alloys having aluminum as the predominant component.

The term "copper-containing material" means (1) copper or (2) alloys having copper as the predominant component.

The term "titanium-containing material" means (1) titanium or (2) alloys having titanium as the predominant component.

5 The term "coact" means the adhesive intimately associates with the treated surface chemistry and/or topography. The chemical association can include various chemical bonding phenomena and surface wetting phenomena. The topographical association can include load transfer between the adhesive and the surface.

10 The term "stainless steel" refers to steel alloys having greater than 10 percent chromium.

The term "galvanized steel" refers to an alloy of iron which has been coated with a layer of zinc, cadmium or other similarly effective metal or
15 metals in controlling the rate of corrosion of the steel itself.

The term "energy beam" refers to one or more electromagnetic radiation beams and/or one or more particle beams effective to modify the surface of a
20 material. An example of an effective electromagnetic beam source in the invention is a laser. An example of a particle beam believed effective in the invention is an electron beam.

The term "material" relates to a solid substance such as a metal, an alloy of metal, a metal composite, a metal laminate, a polymer, a polymer composite such as fiber reinforced polymer and composites comprising metals and polymers, as well as inorganic solids such as ceramics and semiconductors.

Modified surfaces having enhanced bonding characteristics have been observed to have one or more of the following surface modification effects: (a) the vaporization off of the surface of any oil, wax, mold release agent or other such organic compound to produce a surface equivalent to a solvent washed surface; (b) altering the surface of a metal or an inorganic material with the energy beam to produce a diminishment of surface carbon in excess of effect (a) above of at least 20 percent after said altering step as measured by x-ray photoelectron spectroscopy; (c) altering the surface of a metal with the energy beam to vaporize at least 20 percent of the native metal oxide on the surface as measured by x-ray photoelectron spectroscopy; (d) heating the surface with an energy beam to melt the surface; (e) heating the surface with an energy beam to not only melt the surface but also to vaporize it; (f) altering the surface with an energy beam to generate a roughened surface thereby generating load-bearing structures; (g), heating the surface to vaporize inorganic chemicals from the surface as measured by x-ray photoelectron spectroscopy; or (h) altering the alloy composition of the surface as measured by x-ray photoelectron spectroscopy; or (i) increasing the oxide thickness by 20 percent or more after altering the surface as measured by x-ray photoelectron spectroscopy.

The invention is a method for making an article comprising an adhesive bond between at least two surfaces of said article, said method comprising the steps of: (a) placing at least one surface of said article in the path of an energy beam for a duration

effective to modify said at least one surface; and
(b) contacting said at least one modified surface an
adhesive comprising said adhesive bond, said adhesive
of a type effective to coact with said at least one
5 modified surface to produce enhancement of the bonding
characteristics of said adhesive bond.

A preferred energy beam source is a pulse
laser and the specific energy density per pulse at the
surface to be treated preferably is coordinated with
10 the pulse time of the laser. For example, when the
pulse time is between 1 and 100 nanoseconds, the energy
density is preferably between 0.005 and 100 joules/cm²
per pulse and more preferably between 0.05 and
10 joules/cm² per pulse. Generally, a 100 fold change
15 in pulse time requires a corresponding 10 fold change
in preferred energy density.

Another preferred energy beam source is a
continuous wave laser and the specific energy density
per time of treatment duration at the surface to be
20 treated preferably is coordinated with the treatment
duration time for any one point treated on the surface.
For example, when the duration time is between 0.1 and
10 milliseconds, the energy density is preferably
between 5 and 10,000 joules/cm² per duration time and
25 more preferably between 50 and 1,000 joules/cm² per
duration time. Generally, a 100 fold change in dura-
tion time requires a corresponding 10 fold change in
preferred energy density.

Materials beneficially bonded by the method
30 of the invention include polymers, metals and inorganic
materials such as glass.

The invention also includes an article made using the method of the invention.

The invention is also a method for preparing a surface formed of a material of a type capable of being treated to produce an enhanced bondable surface by using the method below, said method comprising the steps of: placing said surface in the path of a beam of electromagnetic radiation having an energy density selected to produce beneficial enhancement of the bonding characteristics of the surface; applying said beam for a duration effective to modify the surface; and applying an adhesive of a type effective to coact with the treated surface to produce a stronger bond than with respect to the nontreated surface.

15 Brief Description of The Drawings

Figure 1 shows an apparatus useful for the method of the invention.

Figure 2 shows photomicrographs of laser treated aluminum of Example 9.

20 Figure 3 shows photomicrographs of laser treated titanium of Example 12.

Figure 4 shows photomicrographs of laser treated silicone rubber of Example 19.

25 Figure 5 shows photomicrographs of laser treated tin of Example 20.

Figure 6 shows photomicrographs of laser treated graphite fiber reinforced epoxy composite of Example 21.

Figure 7 shows photomicrographs of laser treated cold rolled steel of Example 22.

Figure 8 shows photomicrographs of laser treated copper of Example 23.

5 Figure 9 shows photomicrographs of laser treated molybdenum of Example 24.

Figure 10 shows photomicrographs of laser treated tungsten of Example 25.

10 Figure 11 shows photomicrographs of laser treated glass of Example 30.

An apparatus useful for modifying surfaces to be bonded according to the method of the invention is typically illustrated in Figure 1 and involves a laser 10 and means 14, 16 and 26 for guiding the beam from
15 the laser to the surface of the object to be treated. A preferred laser 10 is a Q-switched Nd:YAG laser, but other lasers which are preferred include gas lasers, CO₂ lasers, and excimer lasers. The Kirk-Othmer "Encyclopedia of Chemical Technology," Third Edition,
20 Volume 154, pages 42-81, John Wiley & Sons, New York (1979), describes various types of lasers and their uses. The apparatus of the invention may also comprise one or more lasers or a laser with beam splitting means adapted for the purposes of the invention.

25 The beam 34 issuing from laser 10 can be altered by a harmonic generator 12 capable of reducing the wavelength of the beam proportional to a selected

integral factor, and optical components, such as a prism 14 to spacially separate differing frequencies of the laser beam, a right-angle prism 16, and a preferred cylindrical focusing lens 26 which focuses the laser
5 beam onto a surface to be treated 30 and results in a generally elliptical shaped area of surface treatment at any one time. The length of said ellipse is determined by the diameter of the laser beam and can be made longer by placing a diverging lens, not shown, in the
10 laser beam 34 as is well known in the art. The dotted line 34 between laser 10 and lens 26 can further represent an optical fiber for directing the beam 34 at the surface to be treated.

A power meter 24 can be disposed between the
15 right-angle prism 16 and the focusing lens 26. The power meter essentially has two parts, a detector head 18 integrally connected by means 22 with a conventional analog readout meter 20. The detector
20 head 18 can be placed in the path of the laser beam to detect the average power of the laser beam.

The cylindrical focusing lens 26 is disposed on a translation stage 28. The translation stage 28 includes a track for moving the lens 26 parallel to the path of the beam to focus and defocus the beam at the
25 sample surface 30 to be treated. The translation stage 28 can be manually operated or operated by robotic means or by a motor.

The sample to be treated 30 is disposed on a sample translation stage 32. The sample surface 30 is
30 moved on the translation stage 32 relative to the

beam 34. Preferably, the sample surface 30 is moved perpendicular to the beam 34. The translation stage 32 can be operated by a stepping motor 38 or, alternatively, by a robotic means or by manual means (not shown). Preferably the translation stage 32 is a controlled X-Y translational stage or a combination translation stage-rotating wheel. Such items are easily available commercially, for example, from Velmex Company in Bloomfield, New York. Other means of moving the energy beam relative to the surface to be treated can include optical fibers attached to robot arms that have 2-6 degrees axis of freedom or industrial grade X-Y-Z gantry style platforms. It is convenient to control translation stage 32 with a driver 40 which in turn is operated by a computer 42. The computer 42 can easily control the number of pulses per area or the treatment duration when using a continuous wave laser on the surface 30 and the amount of overlap between successive areas treated may be easily regulated. As long as the energy density for treating the surface is maintained, the relative movement between the laser beam path and the surface to be treated can be as fast as possible. Preferably, each area treated overlaps at least somewhat with the area treated previously. In many embodiments of the invention where there is a visible change in the surface resulting from the laser treatment, it is preferable that there is an overlap of the visibly affected areas from those areas previously treated. In the case of polymer materials, it is generally believed that the depth of apparent vaporization of the polymer is preferably deep enough to (a) remove any mold release agents, (b) roughen the surface, or (c) expose the fibers which can then beneficially interlock with the applied adhesive. Once the

sample 30 has passed through the beam 34, a beam block 36 can be used to trap the beam 34. The invention can also incorporate more than one energy beam, e.g., two or more lasers.

5 The energy beam or beams can be site-specific, that is, focused on a selected area of a surface, such as a metal surface with a high degree of accuracy to insure that the beams do not affect the appearance and/or other characteristics of neighboring surface areas, namely, of
10 areas which do not require any treatment or whose treatment is already completed. The amount of energy transferred to an area of surface may be controlled by focusing or defocusing the energy beam, controlling the exposure time of the beam and adjusting the output power
15 of the energy beam source. Any vaporized material may be easily exhausted from the treatment area using conventional exhaust, so as not to affect the health and/or comfort of the attendants and not to contribute to the pollution of the surrounding atmosphere.

20 The energy beam source must satisfy certain criteria. The first criterion is that the energy beam source must be capable of producing an extremely high energy density at the surface to be treated. For this invention, the critical parameter is absorbed energy
25 rather than incident energy. However, absorbed energy is difficult to quantify and for the case where a laser is used as the beam source, the proportion of energy absorbed varies widely, for example, with differences in the material to be treated and the condition of the
30 surface to be treated. The second criterion is that the absorbed energy must be converted into sufficient thermal

energy to vaporize and/or melt a surface layer of said material or to otherwise modify the topography and/or chemistry of the surface. The third criterion is that the energy beam applied to any specific area of the material must be applied for a relatively short time to control the depth of any melting or charring of the material. This criteria must be observed to prevent melt through or burn through of the material to be treated.

10 Using either a pulsed laser or a continuous wave laser, or a plurality of lasers, the exposure time of the laser onto the object may be used to control the amount of energy directed to the surface of the object. The optimal exposure time and energy content of the energy beam depends upon the chemical composition of the surface of the object, the shape of the surface of the object, the surface roughness of the object, the movement of the surface of the object relative to the beam, the angle the beam strikes the surface of the object, the type of laser being used, and on the ultimate application desired for the object being treated.

25 The preferred type of laser used in the invention depends on the specific application. Among the preferred lasers for metal and polymer surfaces is a Q-switched Nd:YAG laser. Among the preferred lasers for ceramic and polymer surfaces is a pulsed or continuous wave CO₂ laser. It is believed that an excimer laser is also preferred for metal, polymer and ceramic surfaces.

30 Generally when a longer pulse time laser is used, the amount of laser energy focused onto a given

area per pulse needs to be increased. When using a laser having a pulse time between 1 and 100 nanoseconds, preferably the energy density of each laser pulse is in the range of from 0.005 to 100 joules/cm², and more preferably in the range of from 0.05 to 10 joules/cm² per pulse. When using a pulsed laser having a pulse time between 100 and 10,000 nanoseconds, preferably the energy density of each laser pulse is in the range of from 0.05 to 1,000 joules/cm² per pulse and more preferably in the range of from 0.5 to 100 joules/cm² per pulse. When using a laser having a pulse time between 10 and 1,000 microseconds, preferably the energy density of each laser pulse is in the range of from 5 and 10,000 joules/cm² per pulse and more preferably from 50 to 1,000 joules/cm² per pulse. When using a laser having a pulse time between 1 and 100 microseconds, preferably the energy density of each laser pulse is in the range of from 5 to 10,000 joules/cm² per pulse and more preferably from 50 to 1,000 joules/cm² per pulse. Similarly, when using a pulsed laser having a pulse time of 0.1 nanoseconds, it is believed that the preferred energy density of each laser pulse is in the range of from about 0.001 to about 5 joules/cm², and more preferably from 0.01 to 1 joules/cm² per pulse. When using a continuous wave laser, the relative rate of movement between the laser beam and the surface to be modified and the intensity of the beam need to be controlled to similarly achieve beneficial modification. When using a continuous wave laser and a duration of treatment between 0.1 and 10 milliseconds, preferably the energy density is between 5 and 10,000 joules/cm² per duration time, and more preferably between 50 and 1,000 joules/cm² per duration time. When using a continuous wave laser and

a duration of treatment between 10 and 1,000 milliseconds, preferably the energy density is between 10 and 20,000 joules/cm² per duration time and more preferably between 100 and 2,000 joules/cm² per duration time. When using a continuous wave laser and a duration of treatment between 0.001 and 0.1 millisecond, preferably the energy density is between 0.5 and 1,000 joules/cm² per duration time and more preferably between 5 and 100 joules/cm² per duration time. When using a continuous wave laser and a duration of treatment between 0.01 and 1 microsecond, preferably the energy density is between 0.05 and 1,000 joules/cm² per duration time and more preferably between 0.5 and 100 joules/cm² per duration time.

The determination of joules/cm² per pulse is made by interrelating two measurements. The first measurement is a determination of the specific laser beam energy per laser beam pulse. This measurement includes the use of a laser optical power meter as is well known in the art. Generally, laser power meters show the average power of the laser beam in average watts. The number of average watts reported by the laser power meter is divided by the number of laser beam pulses per second to obtain the number of joules per pulse. The pulse time is that time over which about 66 percent of the beam energy is emitted by the laser. The second measurement is a determination of the area on the surface to be modified that is impacted by the laser beam. This measurement is made by placing Zap-It brand laser thermal sensitive paper (Kentek Inc., Manchester, New Hampshire), or an equivalent paper, on the surface to be treated followed by

examination of the resulting visible effect of a single laser pulse. An envelope is drawn around the visibly affected area of the pulse and the area of the envelope is calculated as is well known in the art of geometry.

5 Finally, the number of joules per pulse is divided by the affected area in cm^2 to obtain the joules/ cm^2 per pulse.

The determination of joules/ cm^2 per unit of treatment time for any one point a continuous wave

10 laser is made by interrelating two measurements. The first measurement is a determination of the laser beam power per cm^2 . Using a laser optical power meter, the number of watts reported is divided by the area of the surface treated by the laser at any one time as deter-

15 mined above to obtain watts per cm^2 . The second measurement is a calculation of the duration of exposure of any one point. The width of the treated area in cm at any one time in the direction of surface movement relative to the laser beam is divided by the

20 relative movement velocity in cm per second. Then the watts per cm^2 is multiplied by the treatment duration to obtain the joules/ cm^2 per unit of treatment duration.

The method of the invention can be used for

25 enhancing the adhesion performance of any surface formed of a material of a type capable of being treated with an energy beam to produce an enhanced bondable surface, such as a metallic sheet-forming surface, a polymer or a ceramic. Examples of such a surface

30 include galvanized steel, an aluminum-containing material, or a magnesium-containing material. The

method has been generally observed to enhance metallic surfaces in the tests conducted by the inventors without being limited to a particular metal.

In some applications it is desirable to
5 modify only one surface for enhanced bonding. For example, when bonding dissimilar surfaces, one surface may require modification to enhance its performance to a level approximately equal to the other surface. Additionally, it is sometimes desirable to modify only
10 one surface to predispose a bond to fail in a predictable and beneficial manner not unlike the desire for rolled cellophane adhesive tape to come off its roll with the adhesive layer bonded to only one side of the cellophane.

15 The invention can be used to bond different materials where both surfaces are treated. As an example, it is not generally possible to spot weld aluminum to steel while the present invention can be used to enhance the adhesive bonding of aluminum to
20 steel, galvanized steel to glass fiber reinforced plastic (SMC), aluminum to SMC, and other dissimilar materials generally without limitation.

The specific adhesive used is not critical in the invention as long as said adhesive coacts with the
25 modified surface to produce an enhanced bond. Preferred adhesives which work within the scope of the invention include urethanes, acrylics and epoxies. Other adhesives which work within the scope of the invention include silicone adhesives, cyanoacrylates
30 and thermoplastic hot melts like polyimides. Alternatively, other hot melts, may work within the scope and teaching of the invention.

The specific curing conditions for the adhesive used in the invention are not critical. Generally, the curing conditions are recommended by the manufacturer of the adhesive for a given application. Preferably, the adhesive is applied to the modified surface with a minimum of delay in time. However, tests indicate that when a modified surface was kept covered (in a drawer), enhanced bonding performance was observed even when the adhesive was applied one week and later after surface modification.

With respect to the temperature at which enhanced bonding is proved by lap shear or wedge testing, said testing is generally done at room temperature but can also be done at temperatures higher or lower than room temperature, e.g., at 180°F or at 0°F.

With respect to the examples, the treated surface generally has appeared amenable to a wide variety of adhesives rather than appearing adhesive specific to particular adhesives.

Urethane based adhesives are well known and widely used to adhere plastic and/or metal adherends together. The choice of urethane adhesives over other adhesives is based in part upon their outstanding characteristics with respect to bond strength, chemical inertness, tensile strength and handling characteristics.

One component of a urethane based adhesive generally is an isocyanate-terminated prepolymer compound. Such a compound is normally prepared by reacting a polyisocyanate with a polyhydroxy compound or

other compound containing labile hydrogen atoms that will give a positive Zerewitinoff test. The isocyanate group reacts with the labile hydrogen atom to form a urethane group. A molar excess of the isocyanate is added so that the resulting compound contains free isocyanate groups.

The other component of the urethane based adhesive is generally a cross-linking mixture comprising an admixture of polyhydroxy compound free of isocyanate groups and selected urethane catalysts. When the two components are admixed, for example, in a high shear mixing head and then applied to a surface, a reactive hydrogen can interact with a free isocyanate group chain extended and cross-linked with an isocyanate-terminated prepolymer to form a cured adhesive.

Other adhesives which work within the scope and teachings of the present invention include epoxy adhesives. A variety of epoxy adhesives work within the scope of the present invention including those which are rapidly curable at elevated temperatures and especially adapted for use on automotive assembly lines to adhesively bond metal and/or polymeric parts. Numerous types of epoxy adhesives exist on the market, such as the epoxy described in U. S. Patents 4,459,398; 4,467,071; and 4,485,229. Epoxies and epoxy resins which have increased adhesive strength contemplated for use within the present invention include epoxy resin formulations which are either pure or contain additives which enhance the properties of the epoxy resin. Exemplary enhanced epoxy resin compositions include those described in U. S. Patents 4,002,598; 4,011,281;

4,139,524; 4,146,701; 4,147,857; 4,178,426; and
4,219,638. Curable epoxy resins which are polymerized
by ionic addition mechanisms and often require high
curing temperatures and long setting times can be used
5 within the scope and teachings of the invention.
Essentially, any epoxy adhesive capable of forming a
tight polymer network, characterized by durability,
good adhesion, good water, chemical and/or
heat-resistant qualities can be used within the scope
10 of the invention.

Additionally, combinations of epoxies and
acrylic based adhesives can be used. For example, the
adhesive described in U. S. Patent 3,684,617 dealing
with an adhesive mixture of acrylic based monomer and
15 epoxy resin can be used within the scope of the inven-
tion. Also, a nonreactive composite adhesive described
in U. S. Patent 3,994,764 may be used within the scope
of the invention.

Acrylic adhesives can work within the scope
20 and teachings of the present invention. Acrylic adhe-
sives which include polymers and copolymers formed from
acrylic and methacrylic acids and their derivatives can
be applied to the laser treated surface and provide the
enhanced bonding properties. It is anticipated that a
25 variety of other adhesives will also have utility
within the defined invention. These adhesives include
carboxylic polymeric adhesives, polysulfide adhesives,
phenolic resin adhesives, amino resin adhesives, ethyl-
ene copolymer based hot melt adhesives, polyvinyl
30 acetal adhesives, anaerobic adhesives, polyamide
adhesives and polyethylenimine based adhesives.

These adhesives can optionally contain other materials. Other optional ingredients which can be added to either component include thickeners, stabilizers, flame retardants, metal particles, fibers, fillers, thixotropes and the like. The adhesives which are usable within the scope and teachings of the present invention can be prepared by a variety of methods, e.g., one and/or two-part components using a variety of curing processes.

10 Adhesive materials can in some cases be used in conjunction with a primer as is well known in the art. Here and in the claims such primers are considered to be adhesive materials.

15 The adhesive coating disposed on the surface of the material and treated in accordance with the inventive method, can form a more durable bond, as well as a stronger bond.

20 The invention can be carried out in alternative environments, such as a protective atmosphere composed of nitrogen, or alternatively, an environment containing an inert gas, such as argon or alternatively in an environment containing a reactive gas such as hydrogen. It is contemplated that the inventive method could be practiced in an atmosphere containing a mixture of gases which would enhance the treatment of the surface for enhanced bonding.

25 The novel features which are considered as characteristic of the invention are set forth in particular in the appended claims. The apparatus for the

practice of the method, both as to its construction and its mode of operation, together with additional features and advantages of the method will be best understood upon perusal of the following detailed description of certain specific embodiments with reference to the accompanying drawings as shown in the following examples and comparative examples.

Example 1

The apparatus for treating an object for enhanced adhesion includes a Q-switched Quanta-Ray Nd:YAG model no. DCR-2 laser which produces 30 pulses per second. The laser produces radiation at a wavelength of 1.06 microns with a maximum average power of about 18 watts.

The laser beam is directed at the object to be treated by a system of optical components. The components route and focus the beam. The components are constructed of high quality quartz, S1-UV grade. The beam is directed by 90 degree prisms ESCO model no. 1125250 and focused to a line image about 1/2 inch long by a cylindrical 50 cm focal length lens, ESCO model no. B1-20100.

The objects to be treated, 1 x 4 inch solvent cleaned (the term "solvent cleaned" in this and all examples herein means rinsing three times with methylene chloride unless otherwise indicated) 2024-T3 aluminum alloy panels 1/16 of an inch thick, are placed in a holder on a translation stage synchronized with the laser pulse repetition rate and translated through the beam. The translation apparatus includes a Velmex

Unislide A4000 series translation stage. The slide of the translation apparatus is driven by a stepping motor from Superior Electric, model M061-FD08. The stepping motor is controlled by a Superior Electric model STM 103 controller and the controller is operated by a Commodore 64 computer for complex maneuvers or manually operated.

The panels are translated through the laser beam path at 18 mm/sec and the final 1/2 inch portion of each panel is treated. The lens to panel distance is 35 cm.

Four pairs of panels are treated at each of several energy density levels between 0.14 and 2.16 joules/cm² per pulse. Each panel pair is then bonded together applying a high strength two-part urethane adhesive cured at 135°C for 45 minutes (Dow XPR no. 0544-00923-05-1 urethane adhesive systems) containing 0.5 percent, 0.004 inch diameter glass beads to insure an evenly spaced "glue line" as is well known in the art, only to the treated portion of each panel with a 1/2 x 1 inch lap joint of the panel ends. Table I lists the lap shear strength (measured using ASTM test D-1002) of each panel pair so bonded in relation to laser energy density. The lap shear strength of the panels treated with 0.8 to 2.3 joules/cm² per pulse is about 50 percent higher than those with no treatment. The lap shear strength shown in Table I is an average of four tests and generally such tests show a statistical variation (relative standard deviation) of about ±10 percent. Unless otherwise indicated, all examples herein involved testing in quadruplicate at any one laser energy density treatment.

TABLE ILAP SHEAR TESTING OF LASER TREATED ALUMINUM
PANELS BONDED TOGETHER WITH A URETHANE ADHESIVE

	<u>Laser Energy Density, Joules/cm² per pulse</u>	<u>Lap Shear Strength, psi</u>
5	0	2,300
	0.4	2,200
	0.6	2,500
	0.8	3,300
10	1.0	3,800
	1.2	3,800
	1.7	3,500
	2.3	3,600

Example 2

15 The apparatus of Example 1 is used in
 conjunction with 1 x 4 inch solvent cleaned magnesium
 panels 1/16 inch thick prepared as cold chamber die-cast
 magnesium alloys of type AZ 91B produced by The Dow
 Chemical Company. This alloy contains 9 percent alu-
 20 minum and 1 percent zinc. The sample to lens distance
 is 25 cm..

 The samples are moved through the beam at a
 rate of 15 mm/sec. These magnesium alloy panels are
 then bonded and tested as in Example 1. The results
 25 listed in Table II show that lap shear strength
 increases with increased laser energy density. The
 bond strength increases approximately 60 percent over
 that obtained from the untreated panels.

TABLE IILAP SHEAR TESTING OF LASER TREATED MAGNESIUM
PANELS BONDED TOGETHER WITH A URETHANE ADHESIVE

	<u>Laser Energy Density, Joules/cm² per pulse</u>	<u>Lap Shear Strength, psi</u>
5	0	1,200
	0.1	1,600
	0.3	1,700
	0.4	2,000
10	0.8	1,800
	1.2	2,200

Example 3

The apparatus of Example 1 is used in connection with 1 x 4 inch hot dip zinc galvanized steel panels (Deep DQSK, G-60 automotive grade) 1/32 inch thick. The panels are immersed in a water based oil emulsion, H. A. Montgomery' no. DF-4285 and allowed to drain for a period of 15 to 45 minutes. The panels are translated through the laser beam at 7.4 mm/sec.

20 The sample to lens distance was 50 cm.

These galvanized steel panels are then bonded and tested as in Example 1. The lap shear strength of the bonded panels versus the laser energy density is listed in Table III. Laser treatment in the energy density range of from 1.2 to 5.2 joules/cm² per pulse produced an increase in bond strength of almost an order of magnitude over that of the untreated material.

As the laser power increases to 1.2 joules/cm² per pulse, the lap shear strength increases to about 2,000 psi and remains at about that level for higher laser energy densities. The lap shear strength of non-oiled solvent cleaned panels of galvanized steel is about 1,300 psi.

TABLE III

LAP SHEAR TESTING OF LASER
TREATED OILED GALVANIZED STEEL PANELS
BONDED TOGETHER WITH A URETHANE ADHESIVE

10

	<u>Laser Energy Density, Joules/cm² per pulse</u>	<u>Lap Shear Strength, psi</u>
	0	300
	1.2	1,000
15	1.4	2,100
	1.9	1,700
	2.4	2,000
	2.8	1,900
	3.3	2,100
20	5.2	2,000

Example 4

The apparatus of Example 1 also can be used to improve the durability of bonding. Thirty-two sets of 4 hot dip zinc galvanized steel panels are first pre-treated with an oil emulsion as in Example 3. Two of the panels of galvanized steel in each set are then translated through the laser beam at 7.4 mm/sec using a sample to lens distance of 50 cm and a laser energy

25

density of approximately 1.60 joules/cm² per pulse.
The other two panels of each set are not treated with
the laser and instead are solvent cleaned to remove the
oil. Table IV shows the bond strength of laser treated
5 and solvent cleaned panels bonded together as in Example 1
versus the length of time the panels are exposed to a
moist salty environment in a test known as the General
Motors Scab Corrosion Test. This test is performed
over a period of 32 days and involves testing the lap
10 shear strength of the panels bonded as in Example 1.
This experiment involves 32 cycles, where for each
cycle, the bonded panels are placed for 22.5 hours in a
cabinet with a relative humidity of 85 percent and a
temperature of 145°F, followed by 0.25 hour immersion
15 in a 5 weight percent NaCl solution in water and then
1.25 hours in a dry, room temperature area followed by
a test of lap shear strength. After 7 cycles, the test
results reveal that the untreated panels lost all lap
shear strength and fell apart. In contrast, the laser
20 treated panels maintain a bond for 32 days at a strength
of at least 500-600 psi.

TABLE IV

BOND DURABILITY UPON EXPOSURE TO
MOISTURE AND SALT FOR LASER TREATED AND
SOLVENT CLEANED GALVANIZED STEEL PANELS

5	<u>Days of Exposure</u>	<u>Lap Shear Strength in psi for the Solvent Cleaned Panels^a</u>	<u>Lap Shear Strength in psi for the Laser Treated Panels^a</u>
	0	1,300	2,000
	1	600	1,400
10	4	600	1,400
	7	0	1,300
	14	0	1,300
	18	0	900
	25	0	600
15	28	0	500
	32	0	600

a. Note, these data are the average of 2-3 determinations.

Example 5

20 The apparatus of Example 1 is used in conjunction with hot dip zinc galvanized steel panels (Deep DQSK, G-60 automotive grade) and an acrylic adhesive. (Hardman red/white two-part acrylic adhesive, cured at 325°F for 30 minutes). The galvanized steel panels are

25 treated with an oil emulsion as in Example 3 prior to laser treatment. The sample to lens distance is 35 cm, the sample translation is 15 mm/sec through the laser

beam and the laser energy density is 0.6 joules/cm² per pulse. The oily galvanized panels with no laser treatment before bonding have a bond strength of about 900 psi. The laser treated panels have a bond strength of approximately 1,600 psi. This result represents over a 75 percent increase in bond strength for the laser treated panels bonded with acrylic adhesive in comparison with untreated panels bonded with acrylic adhesive.

10 Example 6

The apparatus of Example 1 is used in connection with treating 1 x 4 inch panels of sheet molding compound (calcium carbonate/glass fiber filled polyester resin containing zinc stearate as a mold release agent) 1/16 inch thick bonded with Hardman red/white two-part acrylic adhesive, containing 0.5 percent, 0.020 inch diameter glass beads, cured according to label directions. The panels are laser treated without any application of oil or other material to the surface of the panels. The lens to sample distance is 35 cm, the sample translation speed is 16 mm/sec and the laser energy density is 0.6 joules/cm² per pulse. Polymer panels bonded without laser treatment have bond strengths of about 100 psi. The laser treated panels show a lap shear strength of about 500 psi. The increase in lap shear strength is greater than 500 percent for laser treated glass fiber filled polymer panels as compared to the untreated panels. Examination of the laser treated surface by x-ray photoelectron spectroscopy indicated that substantially all of the mold release agent was removed by the laser treatment as measured by the diminishment of zinc from the surface after laser treatment.

In addition, 1 x 4 inch panels of acrylonitrile-butadiene-styrene (ABS) plastic sheet, 1/16 inch thick, are laser treated as above and bonded with either a Dow two-part urethane adhesive as in Example 1 cured at 150°F for 30 minutes or bonded with Hardman red/white two-part acrylic adhesive cured at room temperature, containing 0.5 percent, 0.020 inch diameter glass beads, cured according to label directions. The lap shear strength of the laser treated panels is so high that the panels themselves break in testing at about a lap shear strength of 900 psi and for comparison the lap shear strength of the panels without laser treatment is about 400 psi.

Example 7

In Examples 1-6 the test method is ASTM D-1002 for lap shear strength. In this example and in many of the following examples the test method is wedge test ASTM D-3762, modified as described below. In the modified ASTM D-3762 test, 1 x 4 inch metal panels 1/16 inch thick are bonded together with an adhesive and then a wedge is forced between the panels as shown in Figure 3. The initial crack length is a function of several factors including the tensile strength of the bond. The bond strength can be so poor that the test panels fall apart, i.e., an initial crack length in excess of 3 inches. After measuring the initial crack length, the wedged panels, with wedge in place, are placed in a 49°C, 100 percent relative humidity environment for 75 minutes and then the crack growth after exposure (herein termed "crack extension") is measured. If the bond has poor resistance to moisture, then the crack extension can be large and again if large enough the test panels can fall apart. The percent relative

standard deviation precision of the wedge test is generally believed to be about ± 12 percent.

The system of Example 1 is used to laser treat solvent cleaned 2024-T3 aluminum alloy panels. 5 The cylindrical lens is changed to one having a 25 cm focal length and the panels are placed 21 cm from this lens. Between the laser and the cylindrical lens is placed a polarizing filter. By adjusting the polarizing filter, different laser power can be directed 10 upon the panels while operating the laser itself at full power (18 watts).

The panels are translated back and forth through the laser beam at 12 mm/sec to completely treat one side of each panel with about a 150 percent overlap 15 of each pulse treated area. The treated surface of each panel is then coated with American Cyanamid epoxy primer no. BR-127, cured at 250°F for 1 hour and bonded to an identically treated panel with 3M epoxy adhesive no. AF-163-2, OST, Grade 5, cured at 250°F for 1.5 20 hours under vacuum at 100 psi and wedge tested.

As listed in Table V, with no laser treatment the initial crack is about 37 mm and this crack grew about 30 mm upon exposure to moisture. At 0.7 to 1.6 joules/cm² of laser energy per pulse, the initial crack 25 is significantly reduced and the crack grew only about 2 mm to about 5 mm upon exposure to moisture; a significant improvement in both bond strength and bond durability upon exposure to moisture according to the wedge test.

TABLE V

WEDGE TESTING OF LASER TREATED ALUMINUM
 PANELS BONDED TOGETHER WITH AN EPOXY ADHESIVE

	<u>Laser Energy Density, Joules/cm² per pulse</u>	<u>Initial Crack Length, mm</u>	<u>Crack Extension, mm</u>
5	0.0	37	30
	0.7	12	5
	0.8	12	2
	1.1	13	2
10	1.4	12	2
	1.6	12	2

Example 8

This is a comparative example of several prior art surface preparation techniques. Panels of solvent
 15 cleaned 2024-T3 aluminum alloy are sanded with 80, 320 or
 600 grit sandpaper (190, 29 and 17 microns, respectively),
 polished with 5 μ alumina, sandblasted with 54 grit
 aluminum oxide, or wire brushed with 13 mil wire. The
 soxhlet cleaned panels are placed in a Whatman LTD cel-
 20 lulose soxhlet thimble and soxhlet extracted with tol-
 uene for 4 hours (~37 rinse cycles). The panels are
 then coated with American Cyanamid epoxy primer no.
 BR-127 and bonded together with 3M epoxy adhesive no.
 AF-163-2 as in Example 7 and then wedge tested, see
 25 Table VI.

TABLE VI

WEDGE TESTING OF SEVERAL PRIOR ART
SURFACE PREPARATION TECHNIQUES FOR ALUMINUM
PANELS BONDED TOGETHER WITH AN EPOXY ADHESIVE

5	<u>Surface Treatment</u>	<u>Initial Crack Length</u>	<u>Crack Extension</u>
	80 Grit Sandpaper	24 mm	21 mm
	320 Grit Sandpaper	22 mm	22 mm
	600 Grit Sandpaper	17 mm	15 mm
	Polished Surface	49 mm	>27 mm ^a .
10	Sandblasted	15 mm	14 mm
	Wire Brushed	20 mm	15 mm
	Solvent Cleaned	36 mm	>41 mm ^a .
	Soxhlet Cleaned	30 mm	>47 mm ^a .

a: Panels fell apart in the humidity cabinet.

15 The data in Table VI, when compared to the results obtained using the present invention, see Example 7, demonstrate the superiority of the present invention over the surface treatments listed in Table VI as indicated by the wedge test.

20 Example 9

 The system of Example 7 is used to again treat solvent cleaned 2024-T3 aluminum alloy panels except that the polarizing filter is removed and the laser power is adjusted as in Example 1. The panels are placed about 25 cm from the 25 cm focal length cylindrical lens.

The degree of overlap of the area covered by each laser pulse is about 150 percent. The pulse time of the laser depends on the power setting, being about 10 nanoseconds above 6 watts and from 10 to 40 nanoseconds between 1/2 watt and 6 watts, see Table VII.

TABLE VII

PULSE TIME OF THE LASER USED AS A
FUNCTION OF ENERGY DENSITY AND OUTPUT POWER

	<u>Laser Power in Watts/Sec</u>	<u>Laser Energy Density, Joules/cm² per pulse</u>	<u>Pulse Time in Nanoseconds</u>
10	0.5	0.7	40
	1	0.8	25
	2	1.1	20
	3	1.4	16
15	4	1.6	12
	5	1.9	11
	6	2.2	10
	10	3.3	10
	15	4.7	10
20	18	5.5	10

The data in Table VII is provided to allow conversion from laser power to energy density and pulse time for the conditions described above. The following Table VIII shows example data of enhanced bonding characteristics.

The treated aluminum panels are then coated with American Cyanamid epoxy primer no. BR-127 and bonded together with 3M epoxy adhesive no. AF-163-2 as in Example 7 and then wedge tested, see Table VIII.

5

TABLE VIII

WEDGE TESTING OF LASER TREATED ALUMINUM
PANELS BONDED TOGETHER WITH AN EPOXY ADHESIVE

	<u>Laser Energy Density, Joules/cm² per pulse</u>	<u>Initial Crack Length, mm</u>	<u>Crack Extension, mm</u>
10	0.0	40	30
	0.7	19	20
	0.8	12	1
	1.1	12	1
	1.4	11	1
15	1.9	12	1
	2.7	11	3

The data in Table VIII indicate that even at a laser energy density of 0.7 joules/cm² per pulse, the bond strength and durability is improved relative to the nonlaser treated panels.

Figure 2 shows electron photomicrographs of aluminum treated with: (a) a single 0.8 joules/cm² pulse, shown at 3,000X magnification; and (b) an aluminum surface showing overlapping 2.7 joules/cm² pulses, shown at 1500X magnification. These photomicrographs show evidence of surface vaporization and/or surface

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melting along with roughening of the surface. X-ray photoelectron spectroscopy of the treated surfaces listed in Table VIII indicates that even at 0.7 joules/cm² per pulse of laser energy density, the percent carbon on the surface of the aluminum is significantly diminished versus the untreated surface.

Optimization of economic factors using the invention can result from using full laser power with a defocused laser beam to treat a larger area of surface with each pulse. In this event, the linear velocity of relative movement between the laser beam and the surface to be treated can be higher and still effectively treat the surface for enhanced bonding characteristics.

Example 10

The system of Example 9 is used to treat panels of solvent cleaned 304 grade stainless steel. The treated panels are then coated with American Cyanamid epoxy primer no. BR-127 and bonded together with 3M epoxy adhesive no. AF-163-2 as in Example 7 and then wedge tested, see Table IX.

TABLE IX

WEDGE TESTING OF LASER TREATED STAINLESS STEEL
PANELS BONDED TOGETHER WITH AN EPOXY ADHESIVE

Laser Energy Density, Joules/cm ² per pulse	Initial Crack Length, mm	Crack Extension, mm
0	15	22
1.4	17	7
2.7	8	1
5.5	17	3

The data in Table IX show that optimum bond strength as indicated by initial crack length requires a specific treatment power range while bond durability as indicated by crack extension is improved at all laser power levels tested.

Example 11

The system of Example 9 is used to treat panels of solvent cleaned hot dip zinc galvanized steel (Deep DQSK, G-60 automotive grade). The treated panels are then coated with American Cyanamid epoxy primer no. BR-127 and bonded together with 3M epoxy adhesive no. AF-163-2 as in Example 7 and then wedge tested, see Table X.

TABLE X

15 WEDGE TESTING OF LASER TREATED GALVANIZED STEEL
PANELS BONDED TOGETHER WITH AN EPOXY ADHESIVE

	<u>Laser Energy Density, Joules/cm² per pulse</u>	<u>Initial Crack Length, mm</u>	<u>Crack Extension, mm</u>
	0.0	11	2
20	1.4	2	0.3
	2.7	2	0.2
	5.5	4	0.3

The data in Table X show laser treatment improves both initial crack length and crack extension for galvanized steel under the conditions studied. However, it should be noted that the laser treated panels

curled back upon wedge entry and thus the only conclusion believed to be shown by the data in Table X is that laser treatment improved bond strength.

X-ray photoelectron spectroscopy of the 0 and 5 1.4 joules/cm² per pulse treated panels indicates that before laser treatment the surface contains about 70 percent carbon, and that after treatment the surface is essentially 100 percent zinc oxide.

Example 12

10 The system of Example 9 is used to treat panels of wire brushed and nonbrushed solvent cleaned Ti6Al4 titanium alloy. The treated panels are then coated with American Cyanamid epoxy primer no. BR-127 and bonded together with 3M epoxy adhesive no. AF-163-2 15 and then wedge tested, see Table XI.

TABLE XI

WEDGE TESTING OF LASER TREATED TITANIUM
PANELS BONDED TOGETHER WITH AN EPOXY ADHESIVE

	<u>Laser Energy Density, Joules/cm² per pulse</u>	<u>Initial Crack Length, mm</u>	<u>Crack Extension, mm</u>
20	0.0	24 ^a .	36 ^a .
	0.0	20 ^b .	8 ^b .
	1.4	20	4
	2.7	22	4
25	5.5	24	11

a. Not wire brushed.

b. Wire brushed.

The data in Table XI show no improvement in bond strength at the laser powers tested as indicated by initial crack length. However, an improvement in bond durability is seen at 1.4 and 2.7 joules/cm² per pulse of laser energy as indicated by the crack extension data in Table XI.

Figure 3 shows electron photomicrographs of: (a) the titanium alloy before laser treatment at 3,000X magnification; and (b) after laser treatment with a single 1.4 joules/cm² pulse at 2,900X magnification that also shows evidence of apparent surface melting.

X-ray photoelectron spectroscopy of the 0 and 3 watt treated panels indicates that before laser treatment the surface contains about 50 percent carbon and only about 2 percent titanium. After treatment the surface contains about 15 percent carbon and 19 percent titanium (present as titanium dioxide).

Example 13

The system of Example 9 is used to treat panels of solvent cleaned 15 microinch surface ground cold rolled steel. The treated panels are then coated with American Cyanamid epoxy primer no. BR-127 and bonded to an identically treated panel with 3M epoxy adhesive no. AF-163-2 as in Example 7 and then wedge tested, see Table XII.

TABLE XII

WEDGE TESTING OF LASER TREATED COLD ROLLED STEEL
PANELS BONDED TOGETHER WITH AN EPOXY ADHESIVE

	<u>Laser Energy Density, Joules/cm² per pulse</u>	<u>Initial Crack Length, mm</u>	<u>Crack Extension, mm</u>
5	0	20	7
	2.2	22	6
	2.7	24	6
	3.8	23	7
10	5.5	22	7

The data in Table XII show no significant improvement in either initial crack length or in crack extension under the conditions studied. When the solvent cleaned ground cold rolled steel panels are treated as listed in Table XII, bonded using a urethane adhesive as in Example 1 and subjected to the lap shear test, no significant improvement in lap shear strength results. Example 22 describes wedge testing of laser treated cold rolled steel panels and Example 28 describes lap shear testing of laser treated oily cold rolled steel panels.

Photomicrographs of the 5.5 joules/cm² per pulse laser treated ground steel surface showed a general smoothing of the surface, relative to the untreated ground surface, with evidence of overall apparent surface melting.

Example 14

The system of Example 9 is used to laser treat panels of solvent cleaned mirror smooth chrome plated steel. The treated panels are then coated with American Cyanamid epoxy primer no. BR-127 and bonded together with 3M epoxy adhesive no. AF-163-2 as in Example 7 and then wedge tested, see Table XIII.

TABLE XIII

WEDGE TESTING OF LASER TREATED CHROME PLATED
STEEL PANELS BONDED TOGETHER WITH AN EPOXY ADHESIVE

10

	<u>Laser Energy Density, Joules/cm² per pulse</u>	<u>Initial Crack Length, mm</u>	<u>Crack Extension, mm</u>
	0.0	45	13
	0.8	6	0
15	1.4	6	0
	2.7	14	3
	5.5	16	6

The data in Table XIII show that under the conditions studied both bond strength and bond durability are improved by laser treatment as indicated by the wedge test.

20

Example 15

The laser of Example 9 is replaced with an excimer laser having a wavelength of 0.249 micron, a pulse width of about 10 nanoseconds, a pulse frequency of 30 Hertz and a maximum power of 6 watts. The excimer

25

laser is used to treat panels of aluminum, stainless steel and copper at a laser energy density of approximately 10 and 0 joules/cm² per pulse. The treated surface of each panel is then coated with American Cyanamid epoxy primer no. BR-127 and bonded to an identically treated panel of the same metal with 3M epoxy adhesive no. AF-163-2 and then wedge tested. In each case, the laser treatment significantly enhances the bonding characteristics of the panels as indicated by the wedge test.

Example 16

The system of Example 9 is used to treat panels of solvent cleaned 2024-T3 aluminum alloy panels. In this example the Q-switch of the laser is turned off and as a result the laser pulse length is about 100 microseconds. The cylindrical lens is replaced with a conventional converging lens and the laser pulse is focused to a spot 0.6 mm in diameter on the object to be treated in order to compensate for the longer laser pulse length. The translation stage is controlled so that there is about 150 percent coverage of the panel surface with the laser pulses. The treated panels are then coated with American Cyanamid epoxy primer no. BR-127 and bonded to an identically treated panel with 3M epoxy adhesive no. AF-163-2 as in Example 7 and then wedge tested, see Table XIV.

TABLE XIV

WEDGE TESTING OF LASER TREATED ALUMINUM
PANELS BONDED TOGETHER WITH AN EPOXY ADHESIVE

5	<u>Laser Energy Density, Joules/cm² per pulse</u>	<u>Initial Crack Length, mm</u>	<u>Crack Extension, mm</u>
	0	37	39
	140	30	48
	210	15	10

10 The data in Table XIV indicate that significant enhancement of bond characteristics was observed at the highest laser power studied as indicated by the wedge test. This example demonstrates the successful use of a relatively long pulse length laser in the invention.

15 Comparing the data in Table XIV (Q-switch off) with the data in Table VIII and Table VIII (Q-switch on) indicate that delivering a given laser energy density in a relatively short pulse (Q-switch on) is more efficient than a relatively long pulse (Q-switch off).

20 Example 17

The system of Example 9 is used to treat panels of solvent cleaned 2024-T3 aluminum alloy panels. The treated panels are then bonded together with Loctite Super Bonder 495 cyanoacrylate-type adhesive containing
25 0.5 percent, 0.004 inch diameter glass beads to insure an evenly spaced "glue line" as is well known in the art.

TABLE XV

WEDGE TESTING OF LASER TREATED ALUMINUM PANELS
 BONDED TOGETHER WITH A CYANOACRYLATE ADHESIVE

5	<u>Laser Energy Density, Joules/cm² per pulse</u>	<u>Initial Crack Length, mm</u>	<u>Crack Extension, mm</u>
	0.0	54	>23 ^a .
	1.5	36	3

a. Panels fell apart in the humidity cabinet.

10 The data in Table XV show that both the
 initial crack length and crack extension are improved
 with the laser treatment.

Example 18

15 The system of Example 9 is used to treat
 panels of solvent cleaned, Bonderized, (phosphate treated)
 electrogalvanized steel. The treated panels are then
 coated with American Cyanamid epoxy primer no. BR-127
 and bonded to an identically treated panel with 3M
 epoxy adhesive no. AF-163-2 as in Example 7 and then
 wedge tested, see Table XVI.

TABLE XVI

WEDGE TESTING OF LASER TREATED.
 BONDERIZED ELECTROGALVANIZED STEEL PANELS
 BONDED TOGETHER WITH AN EPOXY ADHESIVE

	<u>Laser Energy Density, Joules/cm² per pulse</u>	<u>Initial Crack Length, mm</u>	<u>Crack Extension, mm</u>
5	0.0	8.0	2.2
	0.8	7.6	0.7
	1.4	8.1	0.0
10	2.7	8.2	0.0
	5.5	6.7	0.4

The data in Table XVI indicate that although bond strength was not significantly improved by laser treatment as indicated by the initial crack length, bond durability was significantly improved as indicated by the crack extension under the conditions studied.

Example 19

The system of Example 9 is used to treat detergent washed panels of Duro Inc. 50A red silicone rubber. The test panels are not the usual 1 x 4 x 1/16 inch, but rather are 1 x 4 x 1/8 inch. The treated panels are then bonded together with 3M Scotch-Weld no. 2216 B/A flexible adhesive (3 parts "A" to 2 parts "B" by volume) cured 1 hour at room temperature and 1 hour at 180°F and then subjected to the ASTM D-1876-72 peel test, see Table XVII.

TABLE XVII

PEEL TESTING OF LASER TREATED SILICONE RUBBER
PANELS BONDED TOGETHER WITH SCOTCH-WELD ADHESIVE

5	<u>Laser Energy Density, Joules/cm² per pulse</u>	<u>Peel Strength Pounds per Linear Inch</u>
	0.0	0.1
	1.35	8.3
	5.5	13.6

10 The data in Table XVII indicate that the bond strength as indicated by the peel test was significantly improved after laser treatment.

15 Figure 4 shows 400X magnification electron photomicrographs of silicone rubber: (a) before laser treatment; (b) after overall treatment with 1.4 joules/cm² per pulse of laser energy; and (c) after overall treatment with 5.5 joules/cm² per pulse of laser energy. Figure 4 shows evidence of apparent surface vaporization. Figure 4(c) shows evidence of general overall apparent surface vaporization and roughening.

20 Example 20

The system of Example 9 is used to laser treat panels of solvent cleaned pure tin. The treated panels are then coated with American Cyanamid epoxy primer no. BR-127 and bonded together with 3M epoxy adhesive no. AF-163-2 as in Example 7 and then peel tested using the ASTM 1876-72 peel test, see Table XVIII.

TABLE XVIII

PEEL TESTING OF LASER TREATED TIN PANELS
 BONDED TOGETHER WITH AN EPOXY ADHESIVE

5	<u>Laser Energy Density, Joules/cm² per pulse</u>	<u>Peel Strength, Pounds per Linear Inch</u>
	0	3.6
	1.4	8.9
	2.7	7.0
	5.5	3.5.

10 The data in Table XVIII show that at the intermediate laser energy densities per pulse, the peel strength is significantly improved relative to no laser treatment.

15 Figure 5 shows 3,000X magnification electron photomicrographs of tin: (a) before laser treatment; (b) after overlapping treatment with 1.4 joules/cm² laser pulses; and (c) after overlapping treatment with 2.7 joules/cm² laser pulses. Although there is no significant apparent difference between Figure 5(a) and
 20 5(b), the data in Table XVIII indicates that the surface shown in Figure 5(b) was apparently beneficially modified even though there is no apparent surface melting and roughening of the type shown in Figure 3(b) or Figure 2(a): Figure 5(c) does show evidence of apparent
 25 surface melting and/or vaporization.

Example 21

The system of Example 9 is used to laser treat panels of solvent cleaned aircraft grade graphite fiber reinforced epoxy composite panels, 4 x 1 x 0.040 inches, (60 volume percent Hercules IM-6 graphite fibers, 40 volume percent epoxy resin). The treated panels are bonded together with Hardman blue/beige urethane adhesive, containing 0.5 percent, 0.020 inch glass spheres, and tested for lap shear strength using the ASTM D-1002 lap shear test. Another set of treated panels are bonded together with Hardman yellow epoxy adhesive containing 0.5 percent, 0.020 inch diameter glass spheres, and tested for lap shear strength using the same test. The test results are shown in Table XIX.

TABLE XIX

LAP SHEAR TESTING OF LASER TREATED GRAPHITE FIBER
REINFORCED EPOXY COMPOSITE PANELS BONDED TOGETHER
WITH A URETHANE ADHESIVE OR AN EPOXY ADHESIVE

	<u>Laser Energy Density, Joules/cm² per pulse</u>	<u>Lap Shear Strength, psi Urethane Adhesive</u>	<u>Lap Shear Strength, psi Epoxy Adhesive</u>
5	0.0	2,800	1,845
	1.4	3,020	--
10	5.5	3,010	2,350

The data in Table XIX indicate that the laser treatment resulted in stronger bonds as indicated by the lap shear test for both adhesives at all laser energy densities per pulse studied but with a significant improvement in lap shear strength shown only for the epoxy adhesive. Using the urethane adhesive without laser treatment shows most of the bond failure at the interface between the adhesive and the panel, whereas with laser treatment the bond failure occurred mostly in the adhesive. Therefore, it is believed that the use of a stronger urethane adhesive would have resulted in even higher lap shear test results than shown in Table XIX.

Figure 6 shows electron photomicrographs of the graphite fiber reinforced epoxy composite panels: (a) before laser treatment at 400X magnification; (b) after overlapping treatment with 1.4 joules/cm² pulses

at 400X magnification; (c) after overlapping treatment with 5.5 joules/cm² pulses at 400X magnification; and (d) the same treatment as (b) above but at 3,000X magnification.

- 5 Figure 6(a) shows the graphite fibers just under the surface of the epoxy resin. Figure 6(b) shows the exposure of the fibers, apparently due to vaporization of the epoxy resin around the fibers. Figure 6(c) shows in addition to the exposure of the fibers some apparent
 10 fiber damage that nevertheless does not appear to detract from bonding performance.

Example 22

The system of Example 9 is used to laser treat panels of solvent cleaned mill finish cold rolled steel
 15 (surface not ground). The treated panels are then coated with American Cyanamid epoxy primer no. BR-127 and bonded together with 3M epoxy adhesive no. AF-163-2 as in Example 7 and then wedge tested, see Table XX.

20

TABLE XX

WEDGE TESTING OF LASER TREATED COLD ROLLED STEEL PANELS BONDED TOGETHER WITH AN EPOXY ADHESIVE

	<u>Laser Energy Density, Joules/cm² per pulse</u>	<u>Initial Crack Length, mm</u>	<u>Crack Extension, mm</u>
25	0.0	26	24
	0.8	13	2
	1.4	12	1
	2.7	12	2
	5.5	11	4

The data in Table XX indicate that the laser treatments studied resulted in stronger and more durable bonds as indicated by the wedge test relative to no laser treatment.

5 Figure 7 shows electron photomicrographs of the steel panels: (a) before laser treatment at 400X; (b) after treatment with overlapping 2.7 joules/cm² pulses at 400X; (c) before laser treatment at 3,000X magnification; and (d) after treatment with overlapping
10 2.7 joules/cm² pulses at 3,000X magnification. Figure 7(b) and (d) show apparent surface melting and roughening unlike the surface discussed in Example 13 and it is believed that the roughening shown in Figure 7(b) and (d) may be partly responsible for the improved
15 performance shown in Table XXI with laser treatment.

Example 23

The system of Example 9 is used to treat panels of solvent cleaned copper. In this example the panels are 1/8 inch thick instead of the more usual
20 1/16 inch thickness. The treated 1 x 4 inch panels are then coated with American Cyanamid epoxy primer no. BR-127 and bonded to an identically treated panel with 3M epoxy adhesive no. AF-163-2 as in Example 7 and then wedge tested, see Table XXI.

TABLE XXI

WEDGE TESTING OF LASER TREATED COPPER
PANELS BONDED TOGETHER WITH AN EPOXY ADHESIVE

5	<u>Laser Energy Density, Joules/cm² per pulse</u>	<u>Initial Crack Length, mm</u>	<u>Crack Extension, mm</u>
	0	43	20
	1.4	47	3
	2.7	30	8
	5.5	47	12

10 The data in Table XXI show that optimum bond strength as indicated by initial crack length requires a specific power range while bond durability as indicated by crack extension is improved at all laser power levels tested. In the wedge test, low yield strength materials such as copper require thicker panels (than 15 the usual 1/16 inch thick panels) to prevent the panels from simply curling back as the wedge is inserted between the bonded panels.

20 Figure 8 shows 3,000X magnification electron photomicrographs of the copper panels: (a) after laser treatment with a single 1.4 joules/cm² pulse; and (b) after laser treatment with overlapping 1.4 joules/cm² pulses. Figure 8(a) and (b) show apparent surface melting and roughening after laser treatment.

Example 24

The system of Example 9 is used to laser treat panels of solvent cleaned pure molybdenum. The treated panels are then coated with American Cyanamid epoxy primer no. BR-127 and bonded together with 3M epoxy adhesive no. AF-163-2 as in Example 7 and then wedge tested, see Table XXII.

TABLE XXII

WEDGE TESTING OF LASER TREATED MOLYBDENUM
PANELS BONDED TOGETHER WITH AN EPOXY ADHESIVE

10

	<u>Laser Energy Density, Joules/cm² per pulse</u>	<u>Initial Crack Length, mm</u>	<u>Crack Extension, mm</u>
	0.0	48	a.
	1.4	23	a.
15	2.7	35	a.

a. Panels fell apart in the humidity cabinet.

The data in Table XXII indicate an optimum in bond strength enhancement at an energy density of 1.4 joules/cm² per pulse under the conditions studied as indicated by the initial crack length of the wedge test.

Figure 9 shows 400X magnification electron photomicrographs of the molybdenum panels: (a) before laser treatment; and (b) after laser treatment with 1.4 joules/cm² pulses. Figure 9(b) shows apparent surface melting and roughening after laser treatment.

Example 25

The system of Example 9 is used to laser treat panels of solvent cleaned pure tungsten. The treated panels are then coated with American Cyanamid epoxy primer no. BR-127 and bonded together with 3M epoxy adhesive no. AF-163-2 as in Example 7 and then wedge tested, see Table XXIII.

TABLE XXIII

WEDGE TESTING OF LASER TREATED TUNGSTEN
PANELS BONDED TOGETHER WITH AN EPOXY ADHESIVE

<u>Laser Energy Density, Joules/cm² per pulse</u>	<u>Initial Crack Length, mm</u>	<u>Crack Extension, mm</u>
0.0	62	a.
2.7	47	a.

a. Panels fell apart in the humidity cabinet.

The data in Table XXIII indicate almost exactly a 25 percent reduction in initial crack length after laser treatment.

Figure 10 shows 1,500X magnification electron photomicrographs of the tungsten panels: (a) before laser treatment; and (b) after a single 2.7 joules/cm² pulse. Figure 10(b) shows apparent surface melting and roughening after laser treatment.

Example 26

The system of Example 9 is used to treat 0.006 inch thick solvent cleaned aluminum foil panels. The treated panels are bonded together with Dow Corning Silastic 732 RTV adhesive cured at room temperature for 3 days at 70 percent relative humidity or with 3M Scotch Weld 2216 B/A epoxy adhesive cured for 1 hour at room temperature and 1 hour at 180°F both containing 0.5 percent, 0.004 inch diameter glass spheres, and then peel tested, see Table XXIV.

TABLE XXIV

PEEL TESTING OF LASER TREATED ALUMINUM FOIL BONDED TOGETHER WITH A SILICONE ADHESIVE OR AN EPOXY ADHESIVE

15	<u>Laser Energy Density, Joules/cm² per pulse</u>	<u>Peel Strength Pounds per Linear Inch, Silicone Adhesive</u>	<u>Peel Strength Pounds per Linear Inch, Epoxy Adhesive</u>
	0.0	0.2	8.0
20	1.4	7.2	13.8

The data in Table XXIV show that laser treatment significantly improves bond strength as indicated by the peel test for both adhesives tested.

Example 27

The system of Example 9 is used to treat 0.055 inch thick panels of solvent cleaned Ti6Al4 titanium alloy with overlapping 1.4 joules/cm² pulses.

The panels are bonded together with Langley Research Center Thermoplastic Polyimide primer and adhesive resin and tested for lap shear strength. The primer coated panels are cured for 1 hour at 325°F prior to
5 applying the adhesive to the panels which is heated for 1.5 hours at 625°F under vacuum at 200 psi to bond the panels together. For comparison, additional panels are chromic acid anodized according to aircraft industry standards and bonded together and tested as above. Of
10 all the prior art treatments for titanium alloy, the chromic acid anodizing process is often preferred despite waste disposal considerations for the spent chromic acid bath liquors. The comparative data is shown in Table XXV.

15

TABLE XXV

LAP SHEAR TESTING OF LASER TREATED TITANIUM
PANELS AND CHROMIC ACID ANODIZED TITANIUM PANELS
BONDED TOGETHER WITH A THERMOPLASTIC POLYIMIDE ADHESIVE

	<u>Treatment</u>	<u>Lap Shear Strength, psi</u>
20	Laser	4,640
	Anodized	4,430

The data in Table XXV show that the laser treatment provides a stronger bond than the anodizing treatment but not a significantly stronger bond.
25 Importantly, the data show that the present invention approximately equals the best of the prior treatments for titanium alloy with regard to lap shear testing without a problem of waste disposal of spent bath liquors.

Example 28

The system of Example 1 is used to laser treat panels of oiled cold rolled steel. The panels are bonded together with a urethane adhesive as in Example 1 and then tested for lap shear strength, see Table XXVI.

TABLE XXVI

LAP SHEAR TESTING OF LASER TREATED
OILY COLD ROLLED STEEL PANELS
BONDED TOGETHER WITH A URETHANE ADHESIVE

10

	<u>Laser Energy Density, Joules/cm² per pulse</u>	<u>Lap Shear Strength, psi</u>
	0.0	2,200
	0.8	2,500
15	1.1	3,600
	1.4	4,200
	1.6	5,500
	1.9	4,200
	2.2	5,200
20	2.7	5,000
	3.3	4,200
	4.0	3,200

The data in Table XXVI indicate that above a laser power density of about 1 joule/cm², a significant improvement in bond strength is observed with an apparent optimum in improvement around 2 joules/cm². The lap shear strength of solvent cleaned and nonlaser treated

25

panels is about 4,500 psi. Therefore, the improvements in bond strength shown in Table XXVI are believed to be at least partly attributed to a vaporization of the oil from the surface of the steel with the laser treatment.

5 Example 29

The laser of Example 28 is replaced with a 100 watt (maximum) CO₂ continuous wave laser. The cylindrical lens is removed from the system and the laser beam is instead focused to a spot approximately
10 0.01 inches in diameter. The translation stage is adjusted to move the sample to be treated at a velocity of about 5 inches per second. The laser is adjusted for 50 watt output and thus the energy density of the laser beam directed to any one spot on the sample to be
15 treated is about 160 joules/cm². The duration of exposure for any one spot to be treated is calculated to be about 2 milliseconds.

The above system is used to laser treat
1 x 4 x 1/8 inch panels of plate glass with overlapping
20 coverage of the treated areas (about 150 percent coverage). The laser treated panels are bonded together with Hardman Kalex "Blue Urethane" two-part urethane adhesive with 0.5 percent, 0.020 inch diameter glass beads added to insure an evenly spaced "glue line." This adhesive
25 is recommended by the manufacturer for use with glass and is rated as having a very good resistance to water.

The bonded panels are immersed into boiling water and examined periodically. After 24 hours of this exposure, none of the laser treated and bonded
30 panels fell apart and could not be pulled apart by hand. For comparison, nonlaser treated panels bonded

as above fell apart in the boiling water after 0.6 to 2 hours.

Example 30

The system of Example 29 is used to laser
5 treat 1 x 4 x 1/4 inch panels of plate glass. A
stainless steel, General Motors approved automotive
interior windshield mirror mount is bonded to the laser
treated glass surface with Hardman "Orange" two-part
10 epoxy adhesive (which is recommended by the manufac-
turer for bonding stainless steel to glass and is rated
as having good water resistance) premixed with glass
beads as in Example 29. A 1 x 4 x 1/16 inch carbon
steel panel is bonded to the other side of the glass
panel with the same adhesive as above.

15 The bonded assembly above is immersed into
boiling water for 4.5 hours and then subjected to the
industry specified torque test, i.e., a torque wrench
is attached to the mirror mount and the torque required
to peel the mirror mount away from the glass is measured.
20 The mount could not be peeled away from the glass
without actually breaking the glass (at about 150 inch
pounds of torque) with failure occurring in the glass
itself with no failure at the adhesive/glass interface.
For comparison, a nonlaser treated glass panel was
25 bonded, boiled and tested as above. The mirror mount
cleanly peeled away from the glass at about 70 inch
pounds of torque.

Figure 11 shows electron photomicrographs of
the laser treated glass panels: (a) before laser
30 treatment at 400X magnification; (b) after laser treat-
ment at 100X magnification; (c) before laser treatment

at 3,000X magnification; and (d) after laser treatment at 4,000X magnification. Figure 11(b) and (d) show apparent surface roughening.

Example 31

5 The system of Example 29 is used to laser treat 1 x 4 x 1/8 inch panels of Ashland Chemical Co. "phase alpha" sheet molding compound and the panels are bonded together with Hardman "blue" acrylic adhesive which is recommended by the manufacturer for bonding
10 fiber reinforced plastics. The adhesive is premixed with 0.5 percent, 0.02 inch (0.51 mm) diameter glass beads and the adhesive is cured for 1 hour at room temperature and then at 250°F (121°C) for 1 hour. The bonded panels are tested for lap shear strength which
15 averages 450 pounds per square inch (3.1 MPa) and the panel itself breaks without bond failure. Panels not laser treated but bonded as above have lap shear strengths averaging 160 pounds per square inch (1.1 MPa) and the bond fails at the interface between the
20 adhesive and the panel.

Example 32

 The system of Example 9 is used to laser treat panels of 2024-T3 aluminum at a laser energy density of 1.4 joules/cm² per pulse. The panels are
25 bonded together (1/2 x 1 inch [12 x 25 mm] overlap of the ends of the panels as in a lap shear test) with Hardman "blue/beige" two-part urethane adhesive, containing 0.5 percent, 0.004 inch (0.1 mm) diameter glass beads cured as in Example 31. The bonded panels are
30 then impact tested by General Motors side impact test (modified from the ASTM D-256-81 impact test) wherein the pendulum impact head strikes at right angles to the

bond. The bonded panels show an average impact strength of more than 5 foot pounds. Nonlaser treated panels bonded as above show an average impact strength of 0.4 foot pounds.

5 Example 33

The system of Example 9 is used to laser treat 1/2 x 4 x 0.022 inch panels of gold clad Kovar alloy at a laser energy density of 1.4 joules/cm² per pulse. The gold thickness is 0.0025 inches (24 carat gold). The laser treated gold surface of the panels are bonded together with Dow Corning Silastic RTV-732 silicone adhesive containing 0.5 percent, 0.020 inch diameter glass spheres and allowed to cure for 2 days at room temperature and peel tested at a crosshead speed of 2 inches per minute. The peel strength is 5.5 pounds per linear inch.

Without laser treatment but bonding as above, the peel strength is 2.0 pounds per linear inch.

Example 34

20 A Gentec Model DD-250 TEA CO₂ laser is focused with a spherical ZnSe lens of focal length 100 mm to achieve the energy density indicated in Table XXVII. The pulse length of this laser has a peak including approximately 50 percent of the energy of 25 0.1 microsecond in length. The remainder of the energy is included in a tail approximately 1.0 microsecond in length. The results in Table XXVII indicate no improvement in initial crack, durability, or mode of failure with laser treatment of approximately 5 joules/cm² per 30 pulse.

TABLE XXVII

	<u>Laser Energy Density,</u>	<u>Initial Crack</u>	<u>Crack</u>
<u>Material</u>	<u>Joules/cm² per pulse</u>	<u>Length, mm</u>	<u>Extension, mm</u>
5 Aluminum	0	36.1	34.5
	5.2	34.8	42

Cold	0	40	8.5
Rolled	5.2	40	7.6
Steel			

10 The following will reveal the gist of the
present invention that others can, by applying current
knowledge, be readily adapted for various applications
without admitting features that, from the standpoint of
prior art, fairly constitute essential characteristics
15 of the generic and specific aspects of this contribution
to the art and, therefore, such adaptations should and
are intended to be comprehended within the meaning and
range or equivalence of the appended claims.

1. A method for making an article comprising an adhesive bond between at least two surfaces of said article, said method comprising the steps of:

(a) placing at least one surface of said
5 article in the path of an energy beam having a selected energy density at said surface for a duration effective to modify said at least one surface; and

(b) contacting said at least one modified
surface with an adhesive comprising said adhesive bond,
10 said adhesive of a type effective to coact with said at least one modified surface to produce enhancement of the bonding characteristics of said adhesive bond.

2. The method of Claim 1 wherein said energy beam is generated by a laser.

15 3. The method of Claim 2 wherein said laser is a pulsed laser.

4. The method of Claim 3 wherein said pulse time is between 1 and 100 ns and said energy density is between 0.005 and 100 joules/cm² per pulse.

5. The method of Claim 3 wherein said pulse time is between 1 and 100 ns and said energy density is between 0.05 and 10 joules/cm² per pulse.

6. The method of Claim 3 wherein said pulse
5 time is between 100 and 10,000 ns and said energy density is between 0.05 and 1,000 joules/cm² per pulse.

7. The method of Claim 3 wherein said pulse time is between 100 and 10,000 ns and said energy density is between 0.5 and 100 joules/cm² per pulse.

8. The method of Claim 3 wherein said pulse
10 time is between 10 and 1,000 μ s and said energy density is between 5 and 10,000 joules/cm² per pulse.

9. The method of Claim 3 wherein said pulse
15 time is between 10 and 1,000 μ s and said energy density is between 50 and 1,000 joules/cm² per pulse.

10. The method of Claim 3 wherein said pulse time is between 1 and 100 ms and said energy density is between 5.0 and 10,000 joules/cm² per pulse.

11. The method of Claim 3 wherein said pulse
20 time is between 1 and 100 ms and said energy density is between 50.0 and 1,000 joules/cm² per pulse.

12. The method of Claim 2 wherein said laser is a continuous wave laser.

13. The method of Claim 12 wherein said
25 duration is between 0.1 and 10 ms, and said energy density is between 5 and 10,000 joules/cm² per said duration.

14. The method of Claim 12 wherein said duration is between 0.1 and 10 ms, and said energy density is between 50 and 1,000 joules/cm² per said duration.

5 15. The method of Claim 12 wherein said duration is between 10 and 1,000 ms, and said energy density is between 10 and 20,000 joules/cm² per said duration.

10 16. The method of Claim 12 wherein said duration is between 10 and 1,000 ms and said energy density is between 100 and 2,000 joules/cm² per said duration.

15 17. The method of Claim 12 wherein said duration is between 0.001 and 0.1 ms, and said energy density is between 0.5 and 1,000 joules/cm² per said duration.

20 18. The method of Claim 12 wherein said duration is between 0.001 and 0.1 ms, and said energy density is between 5 and 100 joules/cm² per said duration.

19. The method of Claim 12 wherein said duration is between 0.01 and 1 μ s, and said energy density is between 0.05 and 1,000 joules/cm² per said duration.

25 20. The method of Claim 12 wherein said duration is between 0.01 and 1 μ s, and said energy density is between 0.5 and 100 joules/cm² per said duration.

21. The method of Claim 1 wherein said at least one surface comprises a polymer.

22. The method of Claim 1 wherein said at least one surface comprises a metal.

5 23. The method of Claim 1 wherein said at least one surface comprises an inorganic material.

24. An article comprising an adhesive bond between at least two surfaces of said article characterized by the feature that said adhesive bond was
10 produced by placing at least one surface of said article in the path of an energy beam for a duration effective to modify said at least one surface and applying to said at least one modified surface an adhesive comprising said adhesive bond, said adhesive
15 of a type effective to coact with said at least one modified surface to produce enhancement of the bonding characteristics of said at least one modified surface.

25. A method for preparing a surface formed of a material of a type capable of being treated to
20 produce an enhanced bondable surface by using the method below, said method comprising the steps of:

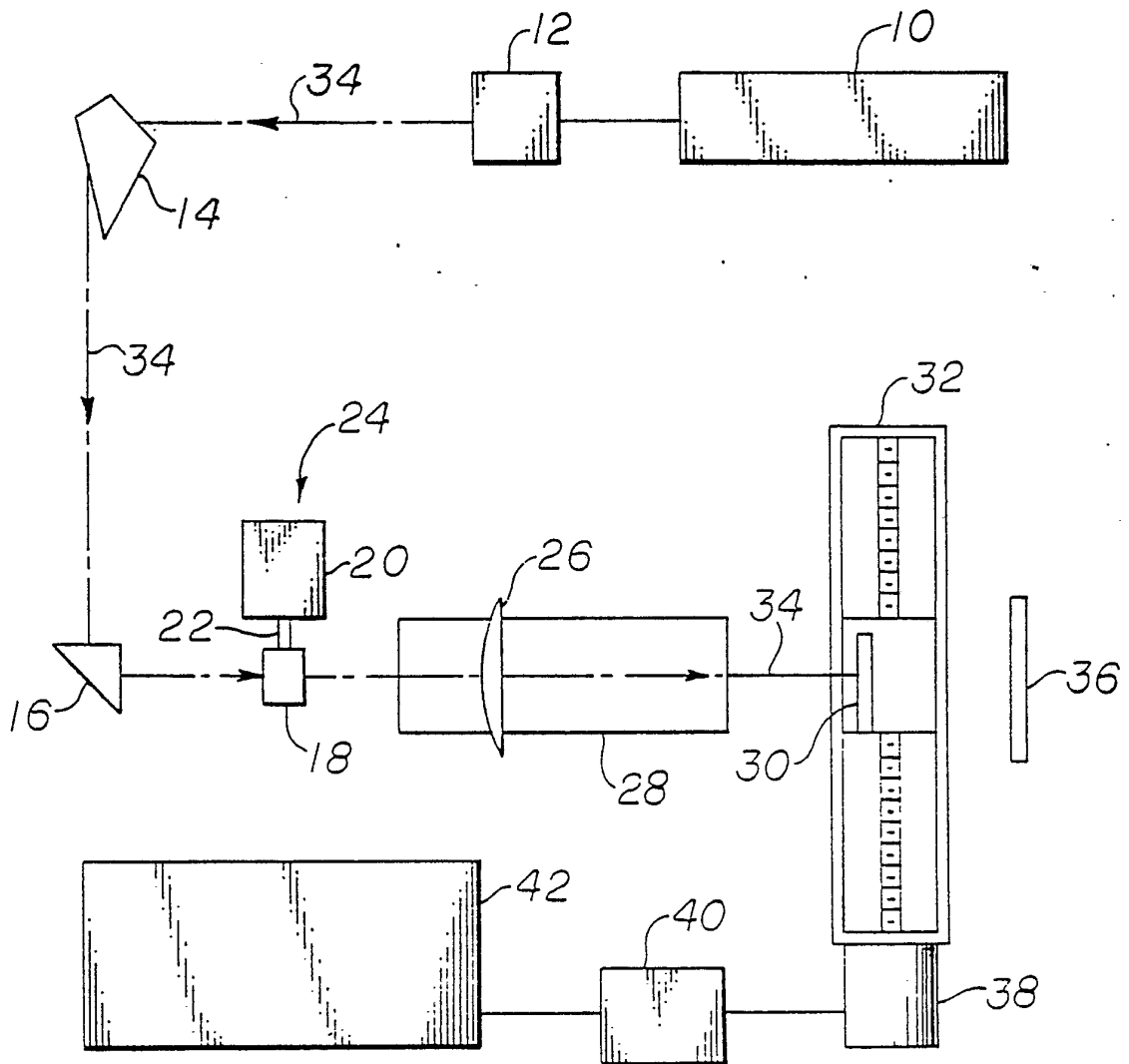
placing said surface in the path of a beam of electromagnetic radiation having an energy density selected to produce beneficial enhancement of the
25 bonding characteristics of the surface;

applying said beam for a duration effective to modify the surface; and

applying an adhesive of a type effective to coact with the treated surface to produce a stronger
30 bond than with respect to the nontreated surface.

26. A method for exposing fibers in a composite material comprising fibers by placing a surface of said composite in the path of an energy beam having a selected energy density at said surface
5 for a duration effective to expose said fibers.

Fig. 1



PHOTOMICROGRAPHS OF LASER TREATED ALUMINUM OF EXAMPLE 9



Fig. 2(b)
1,500X MAGNIFICATION,
OVERLAPPING TREATMENT
WITH 5.5 JOULES/CM² PULSES



Fig. 2(a)
3,000X MAGNIFICATION,
SINGLE 0.8 JOULES/CM² PULSE

PHOTOMICROGRAPHS OF LASER TREATED TITANIUM OF EXAMPLE 12

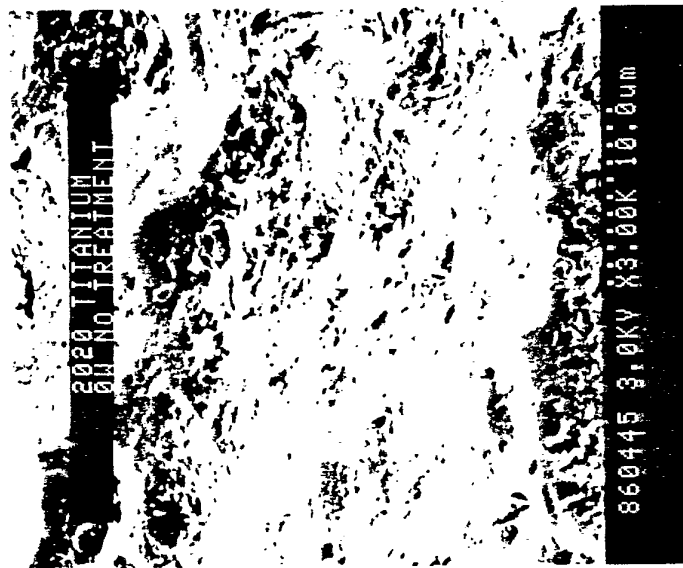


Fig. 3(a)
3000X MAGNIFICATION
BEFORE LASER TREATMENT



Fig. 3(b)
2,900X MAGNIFICATION AFTER
A SINGLE 1.1 JOULES/CM² PULSE

PHOTOMICROGRAPHS OF LASER TREATED SILICONE RUBBER OF EXAMPLE 19

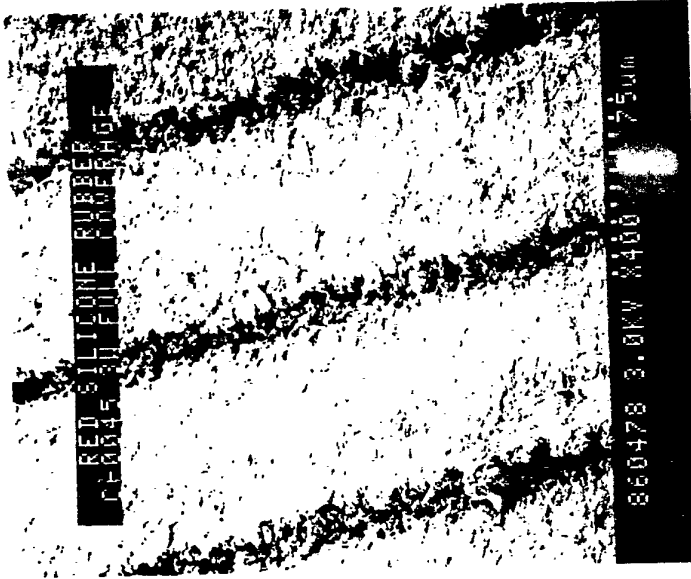


Fig. 4(b)
400X MAGNIFICATION AFTER
OVERLAPING TREATMENT WITH
1.4 JOULES/CM² PULSES

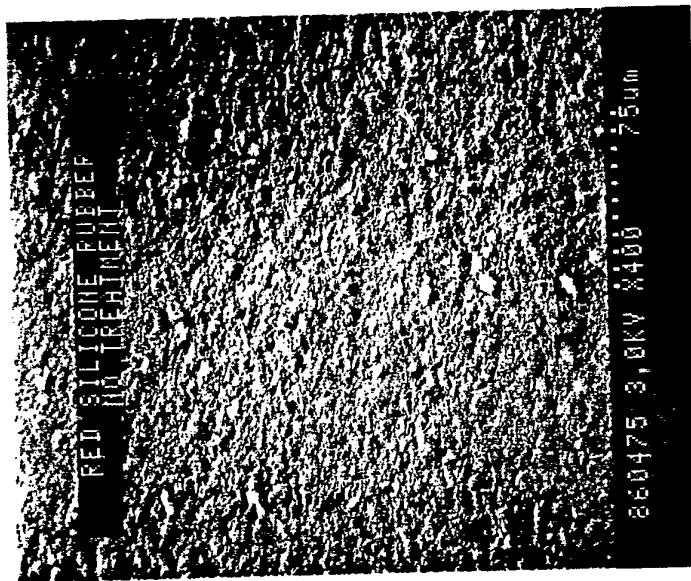


Fig. 4(a)
400X MAGNIFICATION,
BEFORE LASER TREATMENT

PHOTOMICROGRAPHS OF LASER TREATED SILICONE RUBBER OF EXAMPLE 19

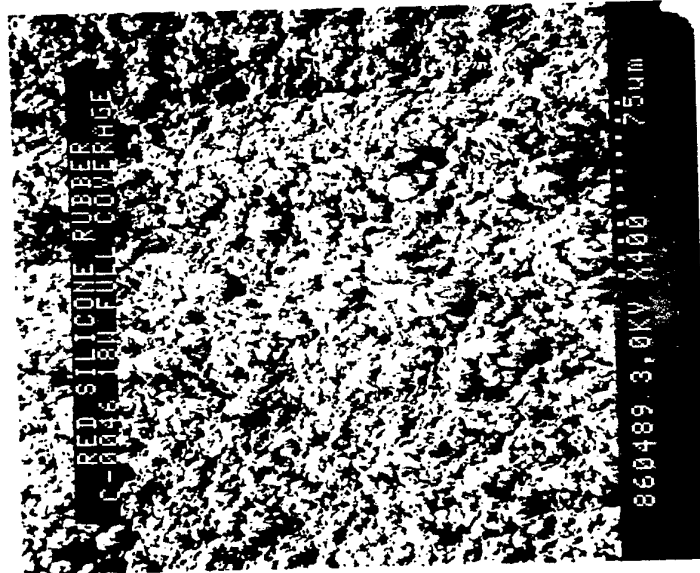


Fig. 4(c)
400X MAGNIFICATION AFTER
OVERLAPING TREATMENT WITH
5.5 JOULES/CM² PULSES

PHOTOMICROGRAPHS OF LASER TREATED TIN OF EXAMPLE 20

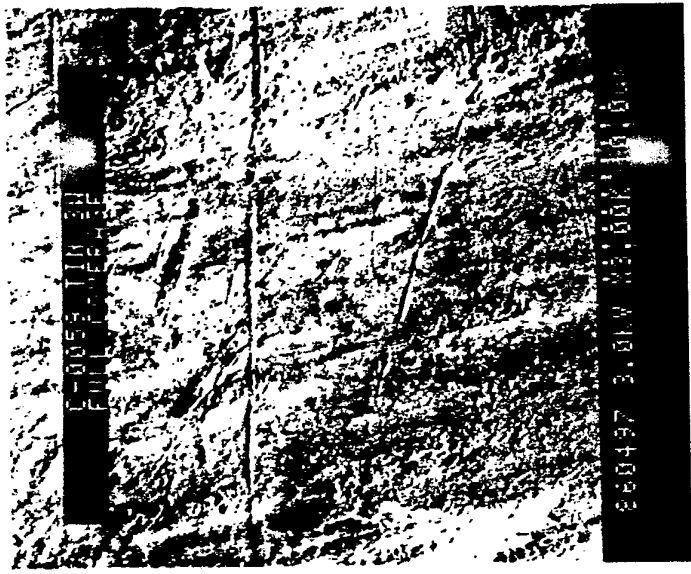


Fig. 5(b)
3,000X MAGNIFICATION AFTER
OVERLAPPING TREATMENT WITH
1.4 JOULES/CM² PULSES

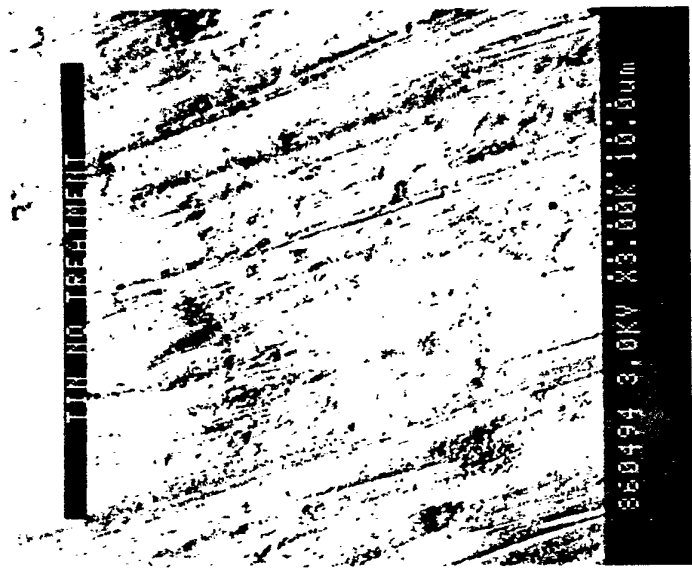


Fig. 5(a)
3,000X MAGNIFICATION BEFORE
LASER TREATMENT

PHOTOMICROGRAPHS OF LASER TREATED TIN OF EXAMPLE 20

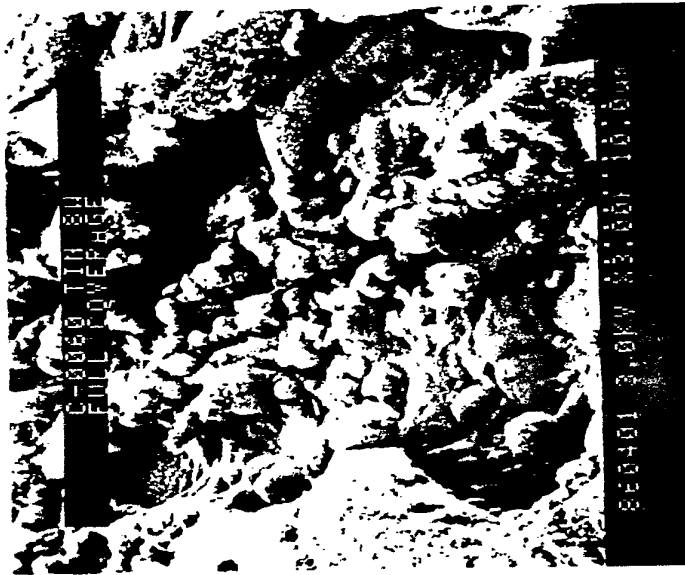


Fig. 5(c)
3,000X MANIFICATION AFTER
OVERLAPING TREATMENT WITH
2.7 JOULES/CM² PULSES

PHOTOMICROGRAPHS OF LASER TREATED GRAPHITE FIBER REINFORCED EPOXY COMPOSITE
OF EXAMPLE 21

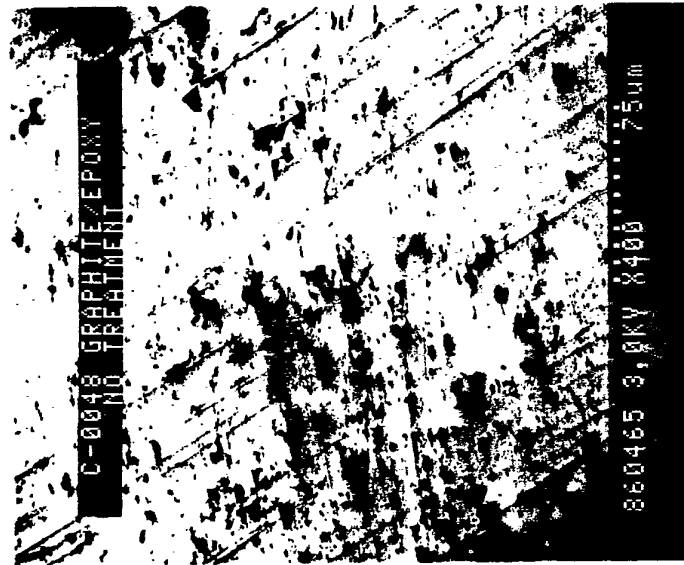


Fig. 6(a)
400X MAGNIFICATION BEFORE
LASER TREATMENT

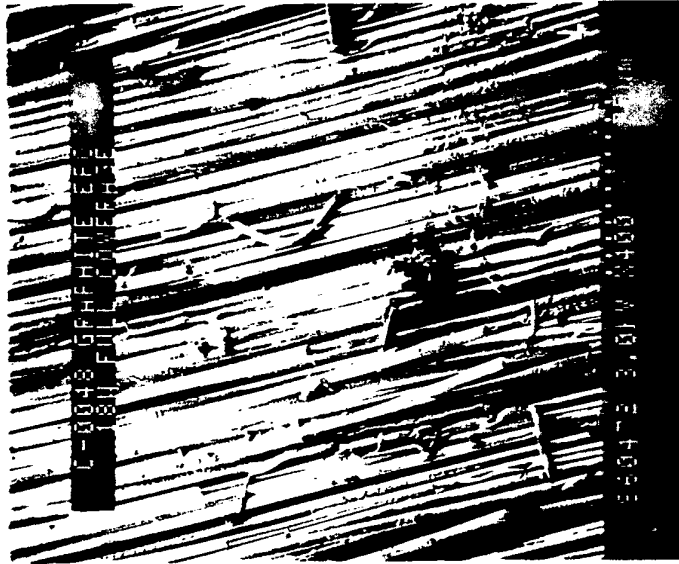


Fig. 6(b)
400X MAGNIFICATION AFTER
OVERLAPPING TREATMENT WITH
14 JOULES/CM² PULSES

PHOTOMICROGRAPHS OF LASER TREATED GRAPHITE FIBER REINFORCED EPOXY
COMPOSITE OF EXAMPLE 21

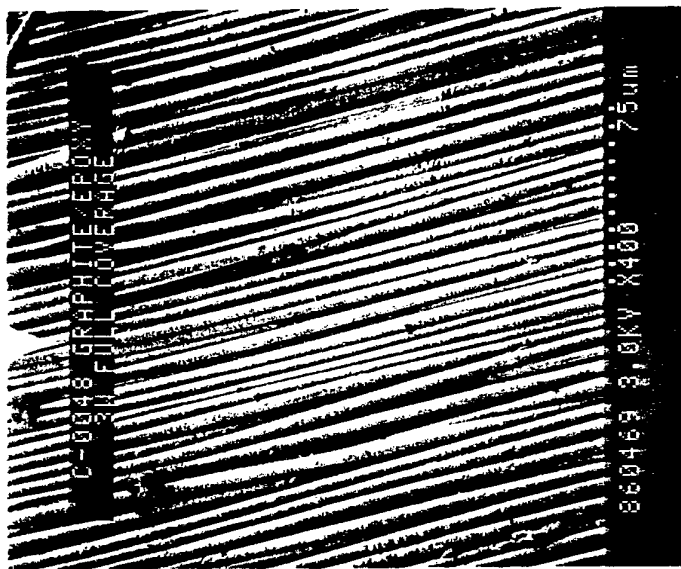


Fig. 6(c)
400X MAGNIFICATION AFTER
OVERLAPPING TREATMENT WITH
5.5 JOULES/CM² PULSES



Fig. 6(d)
3000X MAGNIFICATION AFTER
OVERLAPPING TREATMENT WITH
14 JOULES/CM² PULSES

PHOTOMICROGRAPHS OF LASER TREATED COLD ROLLED STEEL OF EXAMPLE 22

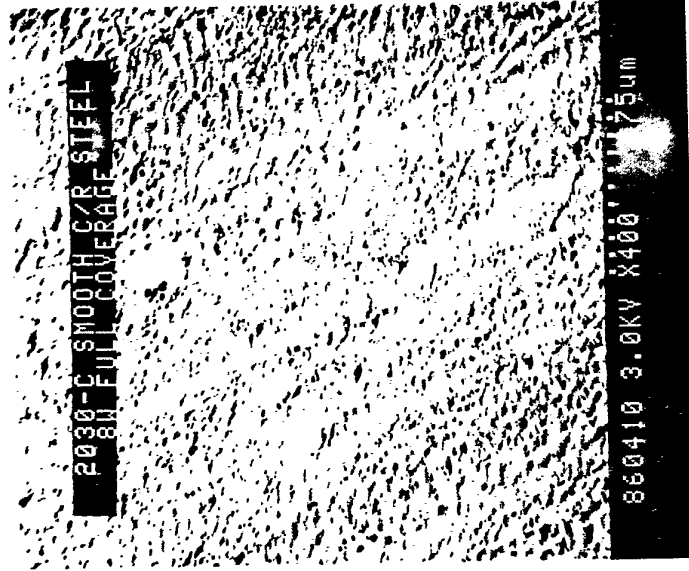


Fig. 7 (b)
400X MAGNIFICATION AFTER
OVERLAPPING TREATMENT WITH
2.7 JOULES/CM² PULSES

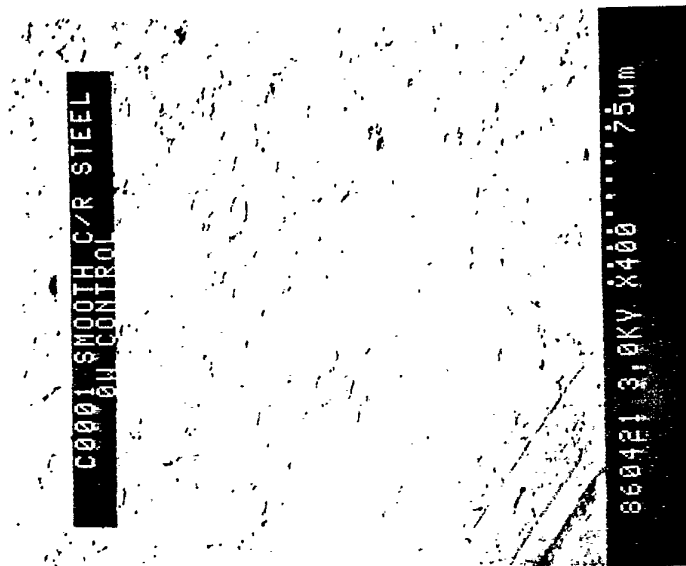


Fig. 7 (a)
400X MAGNIFICATION BEFORE
LASER TREATMENT

PHOTOMICROGRAPHS OF LASER TREATED COLD ROLLED STEEL OF EXAMPLE 22



Fig. 7(c)
3,000X MAGNIFICATION BEFORE
LASER TREATMENT



Fig. 7(d)
3000X MAGNIFICATION AFTER
OVERLAPPING TREATMENT WITH
2.7 JOULES/CM² PULSES

PHOTOMICROGRAPHS OF LASER TREATED COPPER OF EXAMPLE 23

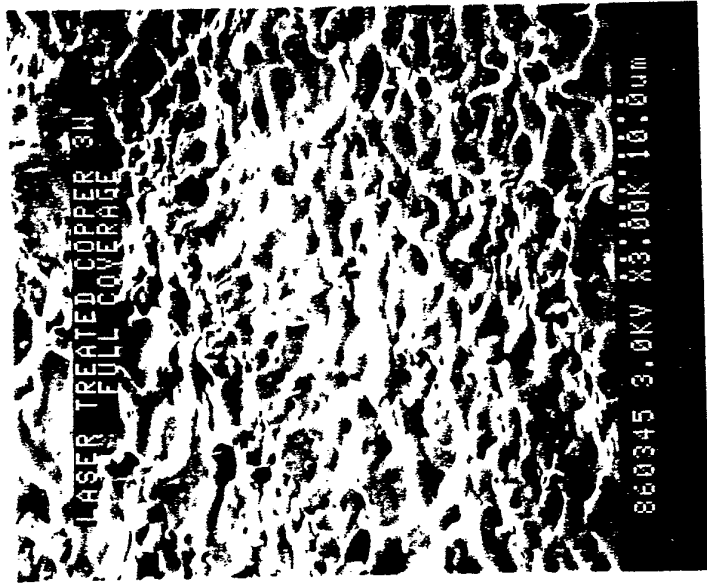


Fig. 8(b)
3000X MAGNIFICATION AFTER
OVERLAPPING 14 JOULES/CM²
PULSES

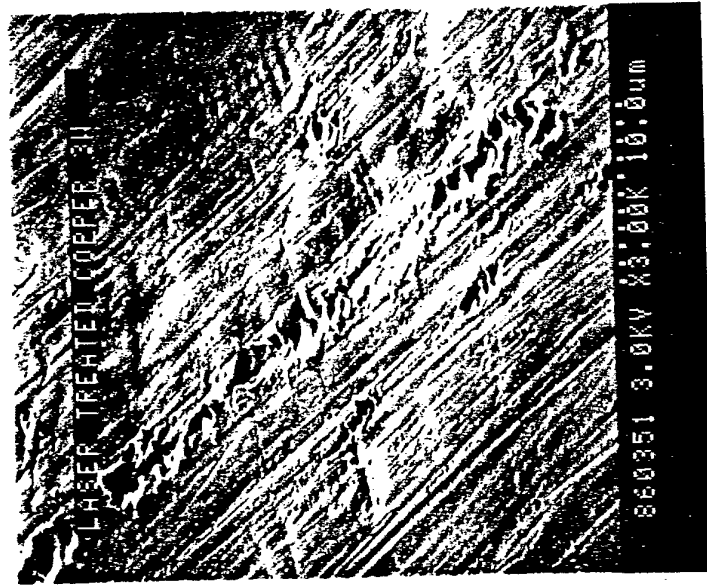


Fig. 8(a)
3000X MAGNIFICATION AFTER
A SINGLE 14 JOULES/CM²
PULSE

PHOTOMICROGRAPHS OF LASER TREATED MOLYBDENUM OF EXAMPLE 24

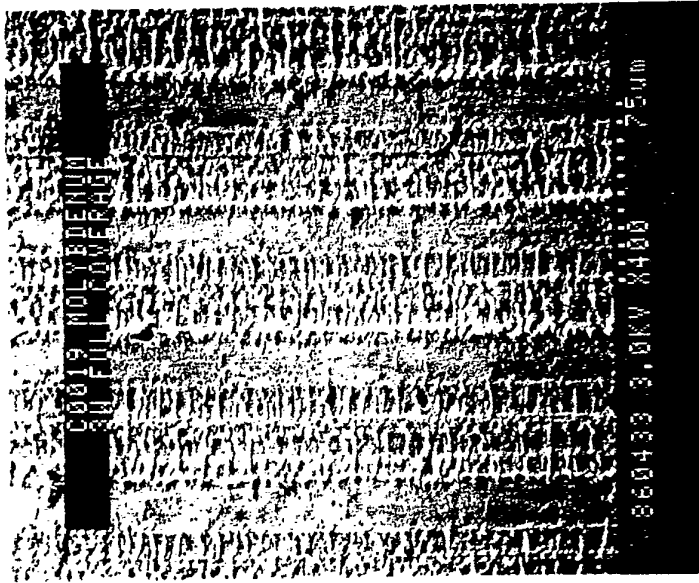


Fig. 9(b)
400X MAGNIFICATION AFTER
1.4 JOULES/CM² PULSES

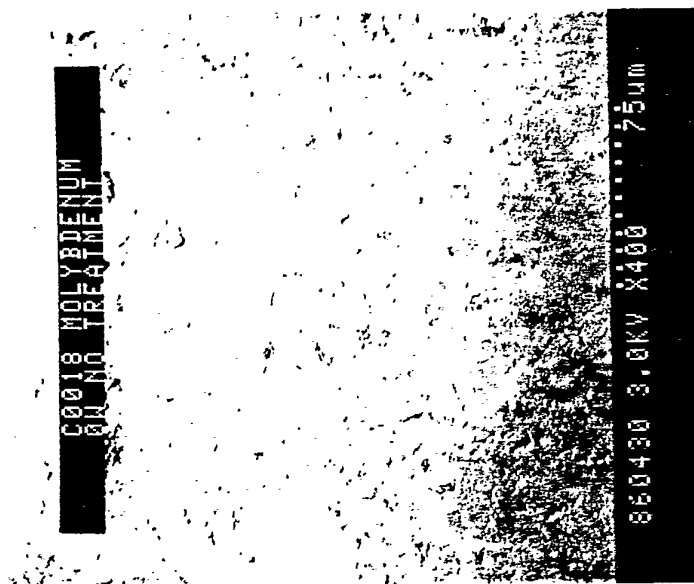


Fig. 9(a)
400X MAGNIFICATION BEFORE
LASER TREATMENT

PHOTOMICROGRAPHS OF LASER TREATED TUNGSTEN OF EXAMPLE 25



Fig. 10(a)
1,500X MAGNIFICATION BEFORE
LASER TREATMENT

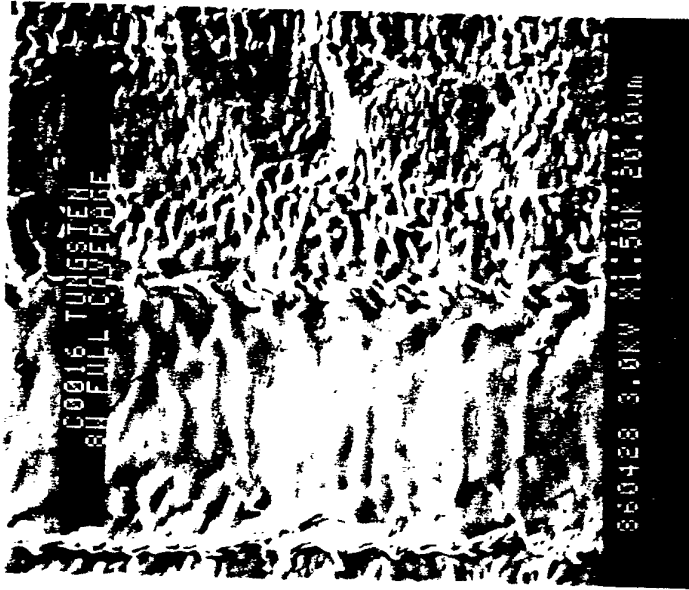


Fig. 10(b)
1,500X MAGNIFICATION AFTER
A 2.7 JOULES/CM² PULSE

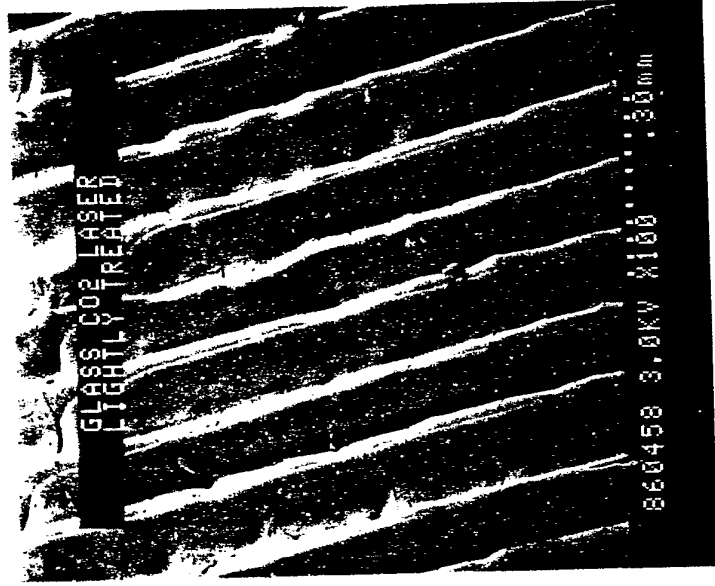
PHOTOMICROGRAPHS OF LASER TREATED GLASS OF EXAMPLE 30

GLASS-UNTREATED



860455 3.0KV X40075um

Fig. 11(a)
400X MAGNIFICATION BEFORE
LASER TREATMENT



GLASS CO2 LASER
EFFECTIVELY TREATED

860458 3.0KV X100300um

Fig. 11(b)
100X MAGNIFICATION AFTER
OVERLAPPING 160 JOULES/CM²
TREATMENT

PHOTOMICROGRAPHS OF LASER TREATED GLASS OF EXAMPLE 30



Fig. 11(c)
3000X MAGNIFICATION BEFORE
LASER TREATMENT

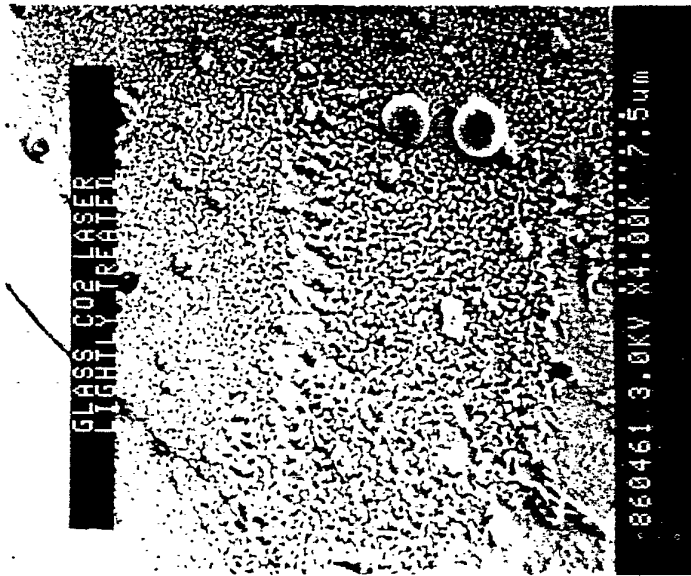


Fig. 11(d)
4000X MAGNIFICATION AFTER
OVERLAPPING 160 JOULES/CM²
TREATMENT

INTERNATIONAL SEARCH REPORT

International Application No PCT/US86/01328

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ³
 According to International Patent Classification (IPC) or to both National Classification and IPC
U.S. Cl.: 156/272.8; 219/121 LF
IPC (4): B32B 31/12, 31/28; B23K 26/08

II. FIELDS SEARCHED

Minimum Documentation Searched ⁴

Classification System	Classification Symbols
U.S.	156/272.8, 272.6, 273.3, 275.1, 275.3, 275.7, 308.2, 308.4, 309.6, 309.9, 390, 153, 155, 643, 634, 535; 219/121L, 219/121LC, 219/121LD, 219/121LE, 219/121LF, 219/121LJ, 219/121LY, 219/121LH, 219/121LH, 219/121LL, 219/121LH; 427/53.1, 54.5; 55; 428/409

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁵

III. DOCUMENTS CONSIDERED TO BE RELEVANT ¹⁴

Category ⁶	Citation of Document, ¹⁴ with Indication, where appropriate, of the relevant passages ¹⁷	Relevant to Claim No. ¹⁸
A	US, A, 3,111,424 (LE CLAIR) 19 NOV. 1963, SEE ENTIRE DOCUMENT.	1
Y	US, A, 3,193,424 (SCOTT) 06 JULY 1965 SEE COL. 1, L 12-57; COL. 4, L 30- COL 5, L 13.	1-26
Y	US, A, 3,560,291 (FOGLIA) 02 FEB. 1971, SEE COL. 1, L 64- COL. 2, L 60; COL. 3, L 59- COL. 4, L 31.	3-11, 21-23, 26
X	US, A, 3,600,289 (BRIGOLE) 17 AUG. 1971, SEE COL. 2, L 23- COL. 3, L 8; COL. 4, L 6-11.	1, 4-21, 24-26
A	US, A, 3,981,762 (DAVIS) 21 SEPT. 1976, SEE COL. 1, L 11-26; COL. 3, L 35- COL. 4, L 34.	1
A	US, A, 4,063,063 (FUNCK) 13 DEC. 1977 SEE COL. 2, L 20-32	1-26
A	US, A, 4,223,074 (YOSHIDA) 16 SEPT. 1980 ^c SEE COL. 1, L 23-55.	1, 25
A	US, A, 4,288,678 (LA ROCCA) 08 SEPT. 1981, SEE COL. 1, L 19-26.	1

¹⁵ 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
- "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

IV. CERTIFICATION

Date of the Actual Completion of the International Search ¹	Date of Mailing of this International Search Report ¹
18 September 1986	25 SEP 1986
International Searching Authority ¹	Signature of Authorized Officer ¹⁹
ISA/US	<i>Merrell C. Cashion</i> Merrell C. Cashion

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, ¹⁶ with indication, where appropriate, of the relevant passages ¹⁷	Relevant to Claim No ¹⁸
Y	US, A, 4,368,080 (LANGEN) 11 JAN. 1983, SEE COL. 4, L 42-58; COL. 8, L 28-40.	1-26
A	US, A, 4,377,736 (DAUNT) 22 MARCH 1983 SEE ABSTRACT.	1
Y,P	US, A, 4,544,442 (LASSEN) 01 OCT. 1985 SEE ABSTRACT.	26