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FIELD REPAIR TECHNOLOGY FOR BATTLE DAMAGE

June 1992

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FINAL REPORT

Contract DAAL04-89-C-0019

Prepared for

U.S. ARMY MATERIALS TECHNOLOGY LABORATORY
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ABSTRACT

The objectives of this research program were to develop a field repair patch for composite armor and composite structures and vehicles which have damaged and restore environmental security and structural integrity quickly and easily. A sunlight cured fiberglass prepreg patch and putty were successfully developed which cured in a few minutes and had excellent physical properties and adhesion to aluminum, steel, FRP, and polyurethane paint. A lightweight portable UV_a photolamp (six pounds) was also developed which is powered by the standard 24-V Army vehicle battery so that the patch and putty can be cured inside the vehicle. The patch and putty is storable inside a sealed aluminum pouch for over 12 months under normal conditions. A NSN number had been assigned for ordering the combined patch and putty field repair system.

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Field Repair Technology for Battle Damage

1.0. INTRODUCTION.

There are continuing requirements for Battle Field Damage Repair(BDR) systems which are: 1) simple; 2) rapidly applied; and 3) effective. The rapid field repair of composite vehicles and armor presents an even more demanding situation, particularly under combat conditions. The immediate repair of vehicles and structures in the field has increased in priority due to the necessity of maintaining the vehicles and structures environmentally sealed in the event of NBC attack, and the need to keep rapidly moving military vehicles continuously operational during missions. Additionally, composites will be increasingly used in U.S. military vehicles in the future as the need to make them lighter, faster, and tougher increases.

The deployment and wide spread use of composite vehicles and composite armor vehicles is now an important thrust by the U.S. Armed forces for the enhancement its mission performance and survivability. In order to maximize the effectiveness of composite vehicles and armor, it must be repaired as soon as possible after receiving damage (as long as it is repairable). A new field repair system was required for these composite vehicles before significant quantities of them are deployed.

Since the field repair must be done under all conditions including battlefield conditions, the repair procedure must also perform under almost all weather conditions that may be encountered from desert to tropical conditions to arctic conditions. Another consideration for the rapid BDR system for composite vehicles, armor, and structures (and any other material) is that the damage to be repaired can consist of irregular holes and cracks, and jagged, torn edges. Sometimes, it is only possible to repair from the inside of the structure or vehicle which is a particularly difficult constraint for the BDR system. Additionally, the system must require a minimum amount of space for application and for storage, be relatively lightweight and be storable with a minimum of six months shelf life under all reasonable field conditions. Even after meeting all of these requirements, it should be relatively low cost (requiring a minimum of tools and special equipment) so that each vehicle has its own repair kit with adequate backup spares available.

In summary, this new rapid field repair system for composite vehicles, composite structures, and composite armor(as well as any such noncomposite structure or vehicle) should meet the following requirements:

1. Simple- A crew member can apply it with a minimum of training and equipment.
2. Rapid - The total time for preparation, application and cure must be a matter of minutes - preferably under ten minutes.
3. Reliable - The system should have a high tolerance to moisture, temperature variation, preparation and application time and yet give good physical properties when cured.
4. Conformable - Easily applied to any shape of crack or hole or surface.
5. Storable - The shelf life should be a minimum of six months under a wide range of conditions.
6. Temperature Insensitivity - It should be useable from -10 to 140°F.
7. Compact and Lightweight - It will be stored aboard the vehicle and the size and weight must be minimized.
8. Low Cost - The lower the cost, the wider it can be deployed and the more effective it can be as an emergency and general repair system.
9. Minimum Working Room - It must require a minimum of equipment and space for application and be able to be applied from the inside of the vehicle or structure.
10. Self Contained - It should require little or no outside power.
11. Good Physical Properties - The physical properties and adhesion are sufficient to restore the repaired area to a satisfactory level of performance until the vehicle or structure is no longer required for the mission situation.
12. One Part Resin System - There is no time for mixing or blending and should not be required in a battle or difficult situation.
13. No noxious fumes - There should be a minimum of noxious when curing or drying.

These requirements are not met by any existing repair system or BDR system for composites except the sunlight cured(UV$_a$) field repair system which Sunrez Corporation developed for this program and field tested in Desert Storm.

All practical reinforced resin or composite vehicle and armor systems have been based on thermoset resins, i.e., epoxy, unsaturated polyesters, phenolic, vinyl esters, and certain cross linked polyurethane systems. These thermosets are usually two part systems and require external heating to complete curing. Unfortunately, the composite vehicle and composite armor which is being repaired is a large heat sink making a thermal cure of a resin very difficult to attain completely. On the other hand if a very sensitive exothermic curing system is used, difficulties in storage and subsequent use by the crew will occur. Current RTV silicone patching systems are easy to use, but do not develop enough strength.

The ideal rapid structural field repair system for composite vehicles and armor (reinforced plastics) will require an easily applied moderate viscosity putty-like resin which requires no mixing(one part) and cures in place in minutes without any addition of heat. Similar two part exothermic thermoset systems are available but require careful mixing prior to use and need post curing (additional heat) especially under cold weather conditions. Additionally, it is difficult to mix a two part system and use glass reinforcing fiber at the same time. The ideal thermoset repair system should cure without heat in the form of a one part prepreg and have excellent shelf life at ambient temperature. The overall structural repair requirements which the Sunrez light cured resin prepreg demonstrated in the Phase I SBIR Program included:

1) Reinforcing fiber--fiberglass.

2) Storable from -40° to 120° F for at least six months.

3) Room temperature cure or lower.

4) Excellent strength on curing.

5) Rapid curing, in a few minutes.

6) Minimum of monomers present, and no solvent.

7) Ease of application from outside or inside the vehicle to be repaired.
8) Inexpensive deployment.

9) Minimum volume/weight storage requirements.

10) Conformable for all repairs of ballistic or other damage.

Sunrez has focused on working with these new fiber glass vinyl ester/unsaturated polyester repair systems which contain a unique photoinitiator to develop the desired BDR system. This photoinitiator is sensitive to weak ultraviolet (longer wavelength) up to almost but not into the visible spectrum. It absorbs between 365 and 410 (nm) which corresponds to commercial tanning lamps. (See Figure 1.) Normal sunlight is very effective in causing a fast cure in minutes.

This new BDR system developed in this program is a one part resin which produces high structural properties when cured with $\mathrm{UV_a}$ light (whether sunlight or a hand held UV lamp) in place to form the repair. In Phase I of this program(DAAL04-87-0062), Sunrez demonstrated the feasibility of the rapid field repair system based on this $\mathrm{UV_a}$ or sunlight cured resin. In demonstrating this feasibility, a prototype resin/fiberglass prepreg was shown to cure at 9° F within ten minutes. All of the basic requirements and goals previously listed were met.

This system is the first available one-part, structural thermoset prepreg which is storable at room temperature of which we are aware. The unique handling characteristics of this new system in being able to do rapid <u>no</u>-heat cures with a hand held UV lamp or by using sunlight permit novel, simple fabrication and repair procedures never available before.

In addition to achieving all goals for Phase I and demonstrating the feasibility of the sunlight cured resin prepreg in Phase I, there were several primary advances with this new repair system. These significant achievements were:

1) Glass filled prepreg can be cured in thick layers up to 0.5 inches thick per layer and achieve high strength composites.

2) The prepregs can be readily handled in normal room light or indirect outside light.

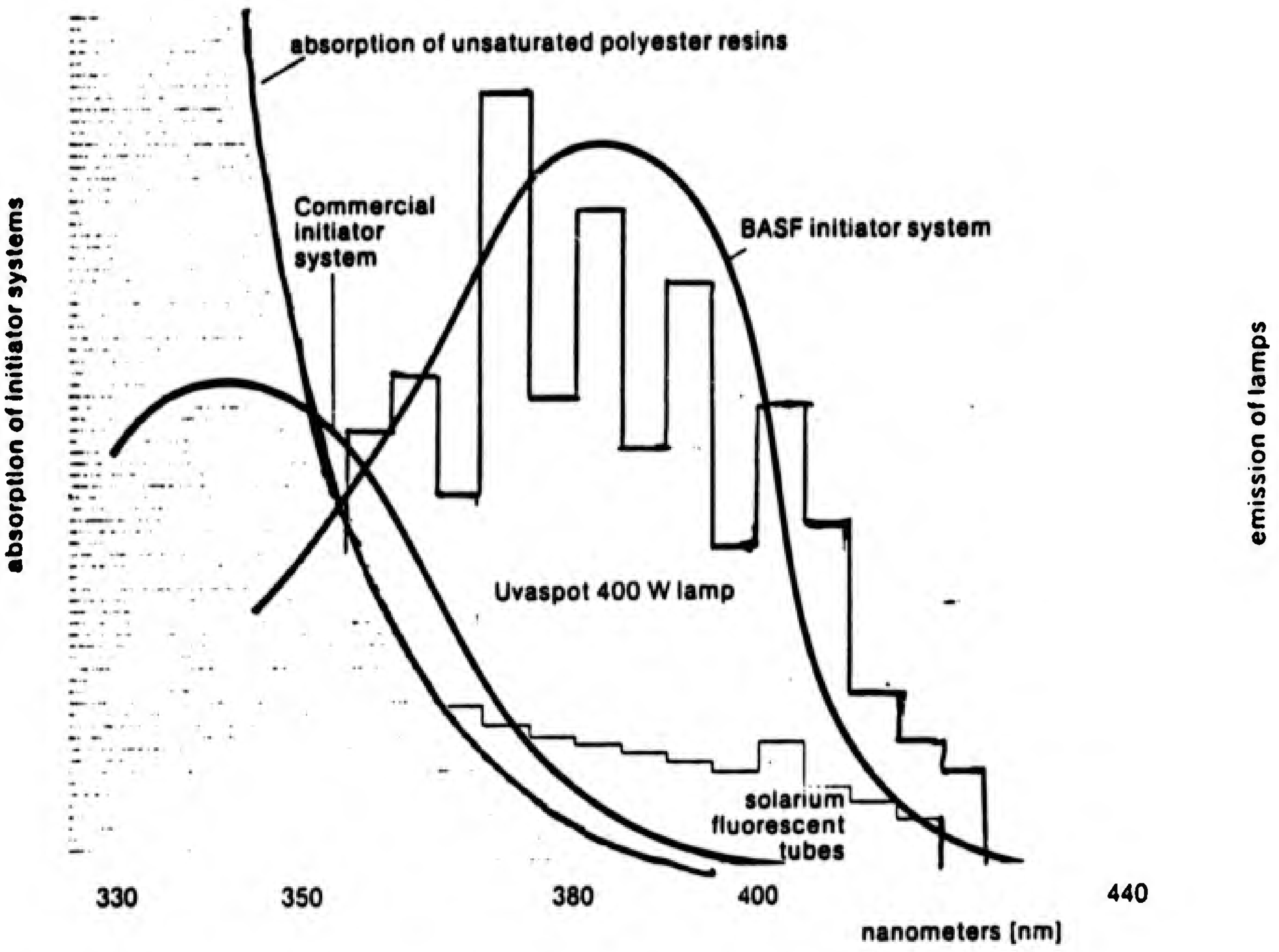
3) The prepregs are room temperature storable and cure readily with sunlight or a hand held UV lamp.

4) A number of American vinyl and unsaturated polyester resins were found to work very well as the primary resin in the formulation.

5) Satisfactory adhesion was obtained between the patch and the surface to be repaired.

FIGURE I

SENSITIVITY OF NEW PHOTOINITIATOR RESIN SYSTEM



Phase II. The overall goal for Phase II of this program was to optimize the resin and patch system with respect to rate of cure, adhesion and physical properties. In addition, the final packaging configuration had to be determined and a compact, portable UV_a lamp had to be designed and fabricated.

Specifically, the goals for Phase II were:

1. To develop a resin formulation which cured as rapidly as possible while maintaining good physical properties through the use special base stock resins;

2. To develop enhanced resin formulations with respect to physical properties including increased damage tolerance (ballistic) which usually means increased elongation;

3. To develop enhanced reinforcements for the patch system including S-2 glass or R glass, and attempt to use Spectra^r and Kevlar^r;

4. To develop the maximum adhesion for the patch system to surfaces including aluminum, steel, polyurethane, epoxy, fiberglass resin surfaces;

5. To develop a portable UV_a lamp which would operate off available vehicle batteries in order to make the patch weather independent;

6. To develop the techniques and approach for patching holes and other types of damage with the patch system;

7. To design the packaging and prepare several sets of patch kits for field trials along with a final report.

These tasks were all accomplished on schedule with some additional results due to the unexpected utilization of the patch system in the Desert Storm Operation.

2.0. DISCUSSION.

2.1. Overview.

The actual technical approach to develop the optimized field repair (BDR) system for composite armor, composite vehicles, and structures proceeded in five technical efforts:

1) Optimized resin development with respect to cure rate and then to properties;

2) Determination of the best reinforcement fibers;

3) Optimization of adhesion to metals and fiberglass resin surfaces with the identification of a putty to form the best bond;

4) Design of the actual patch configuration and packaging along with a commercially viable manufacturing process for the fiberglass prepreg patch along with the inclusion of a container of putty;

5) Design and fabrication of ten portable lightweight UV_a lamps which work off a 24-Volt vehicle battery;

6) Develop repair techniques for the field repair patch system;

7) Field test the field repair system and obtain an NSN number in order to make this BDR available to TACOM and all Government agencies, and submit a final report.

Each of these above technical efforts will be discussed separately in this report. Most of the program effort centered on the optimization of the resin with good success. The detailed experimental results for this resin developemnt are included in the Appendix. All of the above technical efforts were completed successfully and on time. The field repair patch system has been developed, and has achieved commercial status.

2.2. Resin Cure Rate and Physical Properties Optimization.

2.2.1. Approach. Phase I demonstrated the feasibility of using the unique photoinitiator (2,6-di-*t*-butylbenzoyldiphenyl phosphine oxide) with U.S. manufactured blended commercial unsaturated polyester and vinyl ester resins to achieve cure rates of about six to eight minutes with reasonable mechanical properties. In order to practically cure thicker sections as a single cured patch, the fastest curing practical resin is needed which also has good properties. However, the commercial resins used are formulated with the lowest cost materials for peroxide cures, and therefore not formulated or optimized for the Sunrez light cure system. Usually these resins are also highly inhibited with hydroquinones which absorb strongly in the UV including the UV_a (between 360-410 nm) where the unique photoinitiator absorbs and possibly causing slower or poorer curing. Almost in every case these commercially available resins are blended with 30-45% styrene as the monomer and diluent which leaves no opportunity to evaluate the effect of other monomers since the effect of styrene is dominant.

Initially, ten U.S.resin manufacturers were contacted and samples of the appropriate resins were requested if available. The basic focus for these resins were vinyl ester resins and unsaturated isophthalate ester resins. These resins had to meet the following criteria:

1) Low color less than 4 on the Gardener scale--The UV_a range is just below the visible so that absorption in the visible implies strong absorption in the UV_a.

2) Low inhibitor concentration--This is a relative description and usually meant below 0.03% inhibitor by weight.

3) Reasonable physical properties--The key properties were that the tensile strength had to be above 9,000 psi and the elongation above 2%.

The best results from the commercial resins in the light cure formulations provided guidance with respect to which corresponding base stock resin (no monomer and usually low inhibitor added) to request. In many cases the corresponding base stock resin was not available since many of manufacturers considered these base stocks resins proprietary or the base stock resin was not isolated in the manufacturers' particular process. In parallel with the base stock evaluation where possible, samples of many vinyl ester base stock type resins used for coating formulations were obtained from the suppliers, Radcure, Sartomer, Cargill, and RohmTech.

Monomers were obtained from a variety of sources but usually fell into three groups: 1) styrenic type; 2) methacrylate esters; and 3) acrylate esters. These were mixed in proportions from 5 to 45% by weight with the base stock resins and the rate of cure and other effects evaluated.

The overall results from these evaluations provided the criteria for Sunrez to design its own base stock for optimum cure rate and physical properties. Although this base stock would have been made internally by Sunrez, Cargill, Inc. consented to work with us to manufacture the unique resin base stock in their laboratory and then commercially in their pilot plant.

All through these evaluations, the primary criteria was the rate of cure under standardized conditions. When the choices of resins, base stock resins, and monomers had been narrowed down, only those combinations which could also have good physical properties were considered. This also turned out to be all of the base stocks under consideration. The monomers were narrowed to several methacrylate esters and vinyl toluene. (The acrylate esters tended to cure more rapidly, but they usually produced a more tacky surface, and their physical properties were not as good.)

The resin loading in the fiberglass patch was also checked with respect to sufficient tackiness while trying to achieve as high a fiberglass content as possible. This effort was integrated into the effort to optimize the nature of the fiberglass and the fiberglass fabric configuration which is discussed later.

After identifying the best blended resin candidates with respect to cure rate and physical properties and the fiberglass configuration, shelf life was checked with respect to inhibitor level and resin at temperatures up to 140°F.

This approach proved to be the most efficient way to evaluate an almost unbounded matrix of choices in order to select the final base stock being the optimum base stock composition for the targeted application and meeting the given criteria.

2.2.2. Results.

The primary focus of the research of this program was on developing the fastest curing field repair patch possible using a sunlight cured resin. Although Phase I of this program demonstrated that practical cure rates were possible, no development or optimization of resin properties, cure rate, adhesive binding, fiberglass fabrics had been done. We did not know what might be the optimum resin(s).

We evaluated all commercially available vinyl ester resins which were compatible with our photoinitiator along with many unsaturated isophthalate polyester resins and several other "interesting" ones. Since the vinyl ester resins had the best physical properties as a group and exhibited some the best rates of cure, these were selected as the group on which to focus. Although we continued to evaluate new commercial resins as they became available. Over 55 different commercial resins were evaluated. In a parallel effort, all available commercial monomers were evaluated with respect to their effect in combination with a number of commercial base stock resins on the rate of cure and properties. Over 20 different monomers were evaluated. This effort narrowed down our choices to styrene, hydroxypropyl methacrylate, and vinyl toluene. Methacrylate monomers always gave better properties than acrylate monomers although cured slightly slower.

Of the vinyl ester resins, the fastest group with respect to photocuring were the acrylated novolac resins which cured in the range of three minutes. A special light colored epoxy novolac was sent to Cargill Resins who prepared an initial quart sample of the acrylated version of it. The resulting resin(1721) photocured in two to three minutes in 0.25-inch thicknesses under sunlight and was selected as the primary resin for the field repair patch. The backup resins selected were also fast including Cargill 1574 (acrylated epoxy bisphenol A vinyl ester resin) and Dow 411-35 (a methacrylated epoxy bisphenol A vinyl ester resin). The vinyl ester resins also have the advantage over other resins in producing outstanding physical properties including tensiles above 11,500 psi with Barcols from about 40 to over 50 depending on the resin type.

The levels of photoinitiator were varied for different resins and the optimum amount was found to be in the 0.3-0.4% range. The system could tolerate levels of inhibitor such as hydroquinone up to 0.1% without seriously affecting the cure rate or properties on curing. Most additives including the cobalt accelerators normally used for peroxide cured resins slow down the light cure rate and should be eliminated from the resins selected for the basic resin. In fact all resins used should have low color (Gardener = <3).

Having selected 1721 as the primary resin, the optimum amount of monomer and mixture of monomers was determined. The optimum amount of monomers for cure rate appeared to be in the 20-25%. Since the patch would also be used in confined areas, the monomers were narrowed to the two which had the highest boiling point and did not decrease the viscosity of the mix. These two monomers were vinyl toluene(VT) and hydroxypropyl methacrylate(HPMA). HPMA was included to increase surface adhesion of the overall resin mix while the VT was used to maintain elongation and resin properties. The final resin choice was therefore 80% 1721(novolac vinyl ester resin), 10% VT and 10% HPMA. The tensile strength of this resin was over 11,500 with an elongation of 7%. (It was gratifying to find that this resin when exposed to sunlight in the patch did indeed cure in two to three minutes). This photocured one part resin system was equal to or better than epoxies, had a higher T_g (about 300°F), and relatively insensitive to water, solvents, etc.

The use of the multifunctional acrylates such as 1,4-butanediol diacrylate and trimethylolpropane triacrylate was considered, but these increased the viscosity of the uncured resin too much for prepregging the fiberglass fabric and made the cured resin too brittle.

Stability tests of fiberglass patches at 140°F with 0.1% hydroquinone showed that the selected resin system was stable for over three weeks. This would be equivalent to desert conditions for over nine months.

This developed resin more than met our most optimistic goals for cure rate, storability, and physical properties.

2.3. Reinforcement Optimization.

2.3.1. Approach.

The results from Phase I highlighted several problems with respect to the fiberglass and other reinforcements including the nature of the sizing(opaque or transparent), transparency of the reinforcing fiber, the optimized nature of the reinforcement fabric, and the number of layers of reinforcement fabric. The initial effort to try to utilize Kevlar[r] (a UV opaque fiber) even as the bottom layer prevented curing of the resin at the interface. Therefore all reinforcement development effort centered on fiberglass reinforcements. Various available fiberglass materials with different sizings were evaluated, and the best ones selected for optimization of fabric configuration. Although S-2(OCF), R(Vetrotex), and E (from several manufacturers) fiberglass materials were evaluated, the opacity of the available S-2 sizings caused us to focus on the latter two fiberglass materials. As far as the requirements for the field repair patch system, the marginal difference expected in the properties between the R glass and E glass reinforced patches caused us to select E glass fabrics as the preferred reinforcement material. E fiberglass fabrics are significantly lower in cost and are available in a far more extensive range of sizings and styles.

The actual configuration of the fiberglass reinforcement fabric was determined first by estimating the maximum thickness of fiberglass prepreg patch that would cure within eight minutes in sunlight or with the portable UV, light. This appeared to be about 0.25 inches although with the best resin and fiberglass this could be as thick as 0.40 inches. After the overall patch thickness was determined, the thickest available fabric was selected. After attempting to utilize a satin weave which caused many difficulties during impregnation and patch preparation, we were forced to consider only dimensionally stable fabrics with either plain, basket, or twill weaves. In order to maximize bonding between layers (Z-direction) and for adhesion purposes, a thin lightweight nonwoven mat layer was used between each of the three selected 24-oz. plain weave E-glass fabric layers and as the outside layers. The final E glass fabric was purchased sized with a clear sizing such as an aminosilane coupling or bonding agent.

The overall maximum percent glass required in the prepreg patch in order to maintain the necessary flexibility and tackiness and to minimize the amount of air bubbles that formed on flexing was investigated and found to be about 50-55%. Higher amounts of glass up to 65% could be used but at the risk of the prepreg being too dry or forming bubbles due to flexing.

2.3.2. Results.

A specially woven S-2 fiberglass 6-harness fabric with 933 sizing was evaluated for the photocure repair patch. Although the patch cured with three layers of the fabric, it was not transparent enough for the patch application to permit as thick a patch (about eight layers with this fabric) as needed, or about three to four layers of 24-oz. with no significant slow down. A sample of the woven S-2 used in boating applications was also evaluated with the same disappointing result. The glass fabric must be sufficiently transparent for our application. The current nonballistic sizings on R-glass and E-glass were transparent enough for our patch application to permit the 1/4-in thick patch. We elected to use the 24-oz woven roving E-glass fabric because of its ready availability and excellent performance. An excellent highly transparent E-glass fabric was obtained from Fiber Glass Industries, Inc. R-glass will be used when better structural properties are required.

The development and optimization of the reinforcement centered on fiberglass roving and nonwoven mats. This work interacted totally with the development of the prepreg patch and is reported in section 2.5.2.

2.4. Optimization of Resin Adhesion and Adhesive Putty Development.

2.4.1. Approach.

The ease of using this light cured field repair system makes it a desirable choice for the field repair of not only composite vehicles and armor but all such vehicles and structures. The system will cure and adhere on most if not all of the standard materials used in U.S. military vehicles including fiberglass reinforced plastics (FRP), polyurethane paints, polycarbonate, aluminum, and steel. However, although satisfactory adhesion was obtained with the optimized resin patch system with FRP and aluminum surfaces, steel surfaces posed some problems.

Initially, the lap shear adhesive strengths of the two primary candidate patch resins were tested against FRP, steel and aluminum. The preferred acrylated novolac resin(1721) was found to bond better than low inhibited Dow 411(backup candidate) against FRP and aluminum, but less well against steel which general was the most difficult surface for bonding. After establishing these baseline results, various adhesion promoting primers and surface modifiers were investigated with good results. In certain cases, the adhesion promoter was added to the resin itself with good results. However, this caused increased thickening of the resin.

Finally, it was realized that the lap shear strength (the interface) between the patch and the surface was very sensitive to efficient wet out and maintenance of this wet out during curing. In addition, although surface preparation was simple it was critical for reproducible good results. The easiest way to achieve reproducibly good results, eliminate the need for an adhesion promoter, simplify surface preparation and make the overall patch system even more versatile was to utilize a glass filled putty plus the prepreg patch. The putty is used to wet out the clean sanded surface and to present a smooth tacky surface for bonding to the fiberglass prepreg patch. With this approach, the adhesive strength of the putty in combination with the selected acrylated novolac resin was optimized successfully.

2.4.2. Results.

After developing a consistent technique for making lap shear test samples, the adhesion of the selected patch resin 1721 was compared against Derakane 411-45. Both resins showed good adhesion to abraded cured fiberglass resin plates, lap shears over 1800 psi. The problems as expected were with aluminum and steel. Both resins were in the 1000 to 1100 psi range without priming. Priming the aluminum surface with an aminosilane primer increased the lap shear to over 1800 psi. The use of this primer on steel achieved satisfactory lap shears of 1300-1400 psi for both resins.

In order to simplify the priming, the primer was included in the bottom layer of the patch which worked very well. However, after a few days the bottom layer hardened indicating that the resin was curing in the presence of the primer.

One of the problems for achieving consistent wetting (and therefore adhesion) of the surface was to make sure that there was enough excess resin on the bottom of the patch. It was decided that the best approach for simplicity and speed of patching was to incorporate a light curable putty into the patch kit to wet out the surface to which the patch could be stuck prior to curing. The primer would be incorporated into this putty. The putty developed was based on a maleic anhydride/propylene glycol base resin with VT monomer and a ceramic fiber /fiberglass thickener. It was the only putty which was storable long term containing 2% of the aminosilane primer. The lap shear against steel was over 1700 psi and against aluminum was over 2000 psi. This was incorporated into the final patch design.

2.5. Design of Actual Patch Configuration, Packaging, and Manufacture.

2.5.1. Approach.

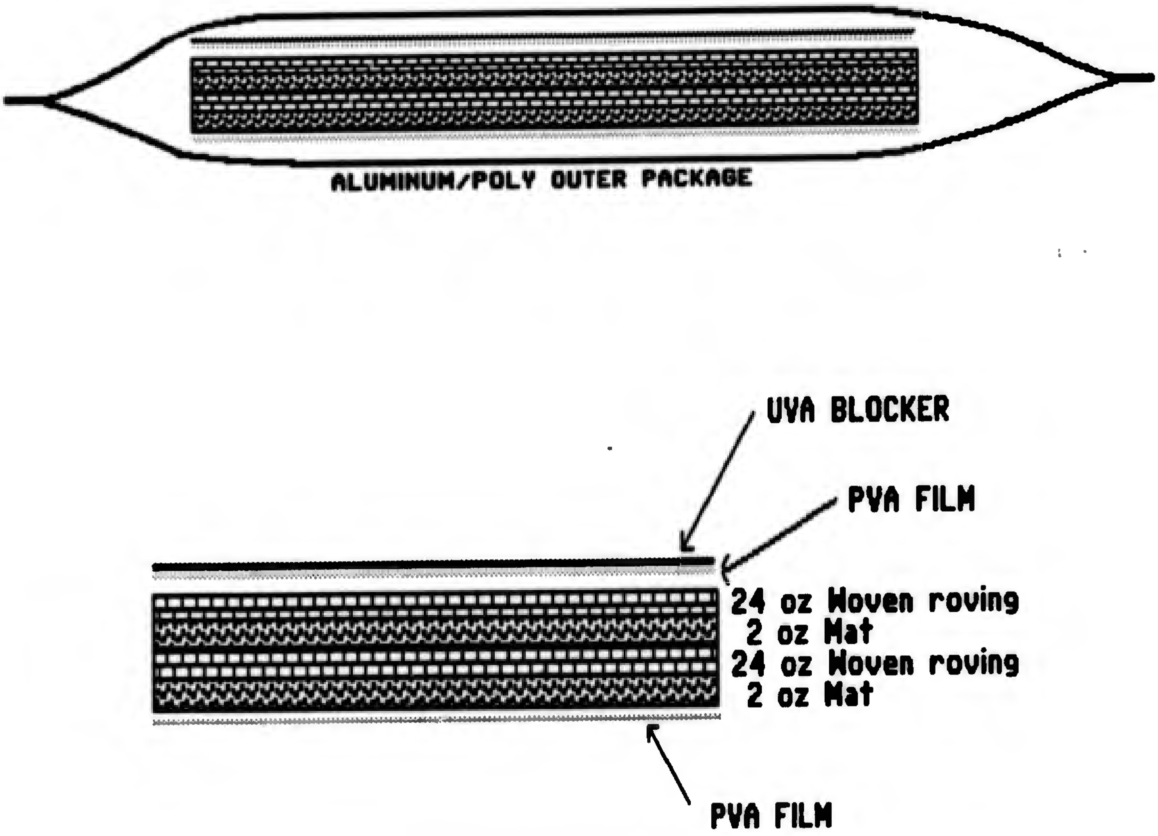
Initially, it was assumed that a slightly different resin system might have to be developed for each type of surface that would be repaired such as FRP, steel, and aluminum. The selection of an adhesive putty plus the prepreg patch as the field repair system permits the use of one field repair patch system for most if not all surfaces. This simplification means that the design of the actual patch package should include both the prepreg patch plus a pouch for the putty. This combination package was adopted for the final patch configuration. In both the putty and the selected resin, it was desired to have as little monomer as possible and have the monomer as high boiling as possible to minimize the amount of solvent vapors in a confined place. Since the patch cures from the outside surface to the interior, most of the monomer vapors are sealed into the patch which is being curing thus lowering the amount of monomer vapor given off.

The actual patch configuration involved solving several problems including the need to prevent sunlight or any light from causing premature curing on storage, the need to enclose the patch in a monomer resistant UV transparent film which functions as the protecting and holding package and finally as the release film during the curing step. An additional need came up during the initial field trials which was that often the protective aluminum pouch was removed in direct sunlight, and the patch started to cure before it was positioned into place. A transparent UV, blocking filter film was needed to permit positioning of the patch before curing and which would be removed to start curing when desired.

All of these factors were systematically incorporated into a final prototype. The final 150 field repair patch kits submitted as a final deliverable for this program were based on this prototype. The cross section of the final patch design is given in Figure II.

During the course of this program in late 1990, TACOM had contacted Sunrez regarding the ordering of ten patches for field trials in the BDR kits for Desert Shield. By the time the order was processed in mid-January for Desert Storm, it had grown to 1000 patches and 5000 containers of putty. (Sunrez was in the process of developing the actual prepreg patch and had identified both the fiberglass fabric configuration and the preferred resins. Additionally, the use of the putty in combination with the patch to achieve maximum adhesion had just been selected as the preferred approach. We were just evaluating the preferred packaging materials and had not selected a good route to manufacture the prepreg and had not developed a packaging procedure.)

FIGURE II
CROSS SECTION, REPAIR PATCH



This order which was shipped in two weeks and on time constituted the actual field trial outside of some preliminary evaluations by TACOM. In addition, a satisfactory manufacturing process was developed and the packaging materials selected and ordered in this time. The patches and putty arrived and were distributed 10 days before the actual ground attack in Desert Storm. This was a real test. Sunrez received a commendation for its on time performance of the Desert Storm Operation from the U.S. Army Materiel Command for this effort. This was the only BDR patch that was deployed in Desert Storm.

Several problems had to be overcome with respect to the manufacture of the prepreg and to securely seal the patches in vapor tight pouches. These problems included:

1) Selection of the appropriate process and equipment for the impregnation of the resin into the multilayers of fiberglass fabric and minimize the retained air or bubbles;

2) The best way to thicken the resin once it was in the prepreg so that it would not run out or shift;

3) The best way to cut and package the prepreg fabric which was worst than double sided flypaper; and

4) The various packaging, transparent UV, release, and sealing films which were stable to the monomers had to be identified, obtained, and proven out.

These problems were solved and the final prototype patch incorporated all of the results.

2.5.2. Results.

In order to make a resin fiberglass prepreg or field repair patch with fiberglass fabric or mat, a thickening process or step must follow the impregnation of the glass with the relatively low viscosity styrene or monomer containing resin. Otherwise the resin tends to run or leak out or moves around in the patch pouch or container. With unsaturated polyesters this is accomplished with the addition of special grades of magnesium oxide followed by very careful heating to effect the thickening action. This process generally does not work on vinyl ester resins because they have no free carboxyl groups to react with the magnesium oxide. However, vinyl resins do have free hydroxyl groups from the acrylation reaction with the epoxide groups when the vinyl resin is made. The addition of several diisocyanates such as toluene diisocyanate or 4,4'-diphenylmethane diisocyanate at 1-3% by weight resin produced the desired level of thickening overnight at room temperature. If the mixture was heated up to 120-150°F for 30 minutes, the same thickening effect was obtained on cooling. The thickened resins photocured as expected in the presence of the urethane type crosslinking caused by the diisocyanates. This approach appears to be general and the thickening is controllable and sufficient for the formation of satisfactory prepregs or patches.

Two new improvements were incorporated into the field repair patch. The first improvement was the use of a textured or dimpled release film for the bottom of the patch in order to increase the resin richness of the bottom face of the patch to increase wet out and adhesion at the interface. The dimpled or textured release film on the bottom would make actual small pockets of resin on the bottom glass fabric face of the patch. (This was not used on the final selected design because of the inclusion of the adhesive putty into the repair patch system.) The second improvement was the addition of a transparent UV, blocking film over the top of the patch or prepreg. This permits the user to work the patch in direct sunlight and provides sufficient working time to position the patch and work out any bubbles which might result from moving the patch over complex contours. After the patch is in place and smooth, the UV blocking film is removed and the patch is cured through the remaining UV transparent release film on the top.

Development of the Final Patch Configuration and Patch Manufacture.

Although the development of a final repair patch configuration and the manufacturing process for it were planned as part of this program, work on this task was accelerated due to an order from TACOM which was received on January 18, 1991 for 1055 patches and 1055 cans of sunlight cured putty for Desert Storm for delivery ASAP. A larger fiber glass fabricating shop and crew was contracted to assist us in the initial scale up. The initial attempt at impregnating the resin into the glass fabric was to lay a layer of 2-ounce mat (50"x30') on the same size of PVA film and wet it out with resin. A corresponding layer of 24-oz. woven roving was then added and wetted out. A second layer of mat was then placed on this stack and wetted out with resin. A final layer of 24-oz. woven roving was then placed on the stack and wetted out. A final layer of PVA film was placed on top of the stack, and the air worked out of the resin/glass patch laminate by hand. The laminate was about 50% by weight resin. This laminate was cut into two 15-foot lengths. One complete half was stacked on top of the other on a long table for cutting into the final individual 10" x 10" patch squares.

This initial scaled-up approach uncovered several problems.

1) It was difficult to wet out the glass layers and then squeeze out all of the air on a large scale. This was partially solved by adding excess resin to the first layer of mat and adding dry woven roving as the second layer and forcing the resin through this second layer from the bottom up. This was done in sequence for the

remaining two layers, but did not work as well as desired because more time was needed to work these last two layers. Making such a large area of resin/glass patch laminate by hand at one time was not beneficial due to the difficulties of working the air out of the laminate. It was decided that the larger size laminate was not beneficial since each man (crew of 10) was actually working against the adjacent men and could not concentrate on a small area.

2) The electrical cutter which we had planned to use quickly became jammed with wet laminate on use. We had to revert to using scissors to cut the large laminate into 10"x10" squares. This turned out to be very messy and left a lot of ragged ends on the side of the patches. It was determined that the glass materials would have to be cut to 10" wide rolls and/or cut into 10" squares before adding resin and stacking up. Alternatively, we could thicken the resin more after wet out and prior to cutting. This would reduce the stickiness and improve the holding ability of the glass mat/roving laminate to eliminate the fiber glass ends that broke loose from the mat.

3) Packaging was initially a disaster. We could not insert the wet resin patches although covered with PVA film into the three sided open aluminum pouches without fouling the closure edge some of the time with drops of resin. Instead of using preformed pouches, we cut the packaging material from a roll of packaging material. The wet patch laminate was placed squarely in one half of this foil sheet and the foil packaging sheet folded in half over the patch to form a pouch. The three remaining unsealed edges of the pouch were then heat sealed to form the pouch containing the square patch laminate. The heat sealable foil packaging material turned out to be too thin and curled too much to form a good pouch for heat sealing. We needed thicker and stiffer packaging material.

We learned that as long as we are doing the impregnation by hand, the material should be of a size that allows the laminator to pay attention to the surface that he is working on at the time. This is no wider than 20" to 30" in width.

We also contracted with Newport Composites to run a test to determine if the patches could be run on a standard epoxy prepreg machine. In operating the machine, it was found that the machinery was set up for a much lower viscosity resin. Instead of the three rollers they normally use to force resin into the fabric, our resin only required one. The pull of this machine was excessive and was squeezing the material far too much as it was wound on the takeup. roll. (The material would spring back as the roll was unwound which caused dry spots.) The mat tended to disintegrate somewhat because of the excessive handling to which this machine subjected the fabric. Roller pressure had to be set very light.

The best method that we finally came up with was to have very light roller pressure and just use one roller. We could not effect enough heating on the impregnated laminate while on the machine to cause thickening of the resin. Finally, we found that if we just wet out the mat/roving by hand and just ran it under a roller, this was sufficient to remove the entrapped air.

On other aspects, we found that a transparent red plastic filter plastic will prevent curing when under UV_a light. We evaluated FEP film as a potential release film to replace the PVA, but no improvement was noted. We evaluated Kapton film as the transparent filter to use on the patch when working in sunlight. It was found to be an excellent material for this application, especially since the color remains fast in the plastic. These features were incorporated in the final delivered patches

Conclusion Regarding Patch Manufacture. This operation will not require a complicated piece of equipment to wet out the material. We obtained a simple impregnating machine which eliminated the hand labor at the wet out step and did a consistent job. The major hurdle is the packaging operation for a production basis.

After shipping the initial order of 1055 field repair patches and 1055 tubes of UV light cured putty to TACOM for Desert Storm and the subsequent order for 5550 tubes of putty, we reviewed our lessons learned and our approach to manufacturing the repair patches. The hardest problem in the operation has been to seal a sticky patch within a gas tight aluminum pouch without fouling the edges to be heat sealed. We determined that a stitched glass stack cut to 10" wide and consisting of two layers of mat and two layers of roving was the best starting material. This material wetted out with the resin as expected in the impregnator and then thickened with the reacting diisocyanate(2%) after impregnation into the glass fabric as expected.

The final patch configuration was the incorporation of the stitched glass prepreg covered with a PVA protecting film and the transparent Kapton UV blocker, along with the additional pouch of adhesion promoted putty into one package.

The resin composition of the patch was finalized as noted previously with the acrylated epoxy phenolic novolac (1721) from Cargill with 10% vinyl toluene and 10% hydroxypropyl methacrylate. The cure rate of the patch in direct sunlight is about two minutes.

The initial optimized patches were shown at the AMC\CASCOM meeting on June 24-26, 1991

2.6. Design and Fabrication of Ten Portable UV$_a$ Lamps Which Function Off of a 24-V Vehicle Battery.

2.6.1. Approach.

Although the primary emphasis for curing the light cured field repair patch and putty is sunlight, a simple field method was needed for light curing the patches under all conditions including the inside of vehicles. Therefore, it was necessary to develop a lightweight portable UV lamp which could work off the best available field power source, the standard 24-V U.S. Army vehicle battery. In order that this unit not be considered cumbersome, it had to weigh as little as possible (under eight pounds), take up a minimum amount of room, and be able to cure the 0.25-in. prepreg patch within ten minutes.

The technical problems to be solved included:

1) Identification of the type of bulb and the minimum size of this bulb that would cure the field repair patch fast enough;

2) Designing a combined inverter and transformer to efficiently convert 24 Volt DC power to 110 Volt AC power(as it turned out) without overheating when left on for up to an hour;

3) Designing a means to keep this combined inverter-transformer light weight and cool;

4) Evaluation and modification of the this combined inverter-converter to cure the field repair patch in the required time for a 10" x 10" area;

5) Modify the system to prevent the vehicle battery from being run down to below minimum vehicle startup up power; and

6) Work out final packaging and build ten units for deliverables under this program.

2.6.2. Results.

Various UV$_a$ photolamps were considered. The lamp which we finally picked was a mercury vapor lamp for its lighter weight, ruggedness, and dependability. The power requirements were set at 100-watts to minimize the weight of the supporting electronics and still be able to achieve a photocure in less than 5 minutes for an area greater than 10" x 10". The required supporting equipment was narrowed to a combined inverter/transformer/ballast all in one solid state board. This would have to convert 24 V DC to 110 V AC. This was developed by Centerset, Inc. The total weight of the entire system including the lamp and 20-ft cord was under six lbs. and used a Spectronics 100-watt mercury flood lamp. After solving the problem of keeping the electronic box cool, the system was then adjusted to function between 21-28 Volts in order not to drain the vehicle battery below the critical voltage necessary to start up the vehicle.

This package successfully cured the field repair patch in five minutes in a 12-inch circle. This lamp could be left on for at least an hour with no adverse effects. All goals were successfully achieved or exceeded.

The first unit was demonstrated with a 24-Volt battery at the AMC/CASCOM meeting " Supporting the Battlefield of the Future" on June 24-26, 1991.

The portable photolamps(10) were assembled and were shipped out to W. Haskell III (AMTL). The whole unit with a 20-ft cord weighed six pounds. The unit has met all criteria assigned to it. The completed lights were shipped without a plug since that will depend with which military vehicle outlet will be used.

2.7. Development of Repair Techniques for the Field Repair Patch.

2.7.1. Approach.

The primary damage that composite and non-composite vehicles and structures will receive under field conditions will probably come from shrapnel or bullets under combat conditions and from accidents under both combat and general training or deployment conditions. (Other types of damage will also occur, but the repair of these will be left to the person in the field or a subsequent technical write up if needed.) Several samples of composite armor which had been penetrated by bullets were repaired. These included samples which were also delaminated. Other repairs which were demonstrated included the repair of a HMMV hood which had been cracked by stepping on it, a nylon gas tank, and a windshield. The experience and lessons learned from these repairs, and the extensive knowledge of Sunrez(Mark Livesay) in composite fabrication and repair has provided the guidelines and overall repair procedures described in the results section below.

2.7.2. Results.

A set of of repair instructions has been prepared for using the field repair patch. These instructions are grouped as:

1) Structural repair;

2) Environmental repair;

3) General procedures.

These instructions are on the next four pages.
(pages 27-29)

INSTRUCTIONS ON USING THE SUNREZ FIBERGLASS REPAIR PATCH.

This patch can be used over a variety of materials including fiberglass structures and parts, other composite parts (Carbon/epoxy, Kevlar/epoxy and etc.), Aluminum, and Steel.

The construction of the patch is as follows: **(Fig 1)**

TOP
Yellow UVA light blocking film
Top clear plastic covering
Fiberglass patch
Bottom clear plastic protective covering
BOTTOM

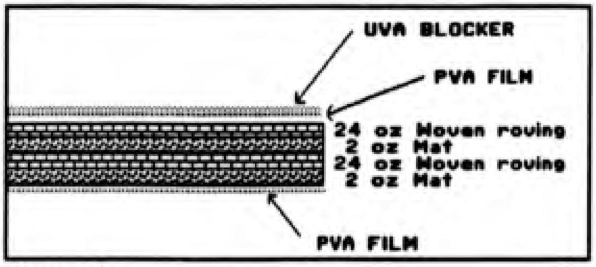


Figure 1

The patch is packaged in a light proof aluminized package.
Putty is packaged separately in light proof 8-ounce bottles.

The top film is left in place until the patch is ready to be cured. This film will block all of the UVA light so that the patch will not cure prematurely. This allows the personnel using the patch to take as much time as necessary to form the patch to the surface to be repaired. The patch will start curing within minutes of the removal of the Yellow film in the presence of UVA light.

The bottom film is always removed unless the patch is used to take the shape from another part. This can be accomplished because the bottom film acts as a release agent for the patch. If the patch is used to copy a shape the bottom and top clear films are left in place and only the yellow film is removed when the patch is ready to be cured.

After curing both the top and bottom films are removed and the part is trimmed if necessary.

It should be determined whether the patch is to act as a environmental repair or a structural repair as the preparation procedures are different for each.

ENVIRONMENTAL REPAIR:
A environmental repair takes less time to repair the surface.

Environmental repairs are meant to be very quick and little attention is given to structural considerations. A environmental repair is meant to seal a structure from the elements and the patch would not have any structural requirements. For environmental repairs, ragged holes are OK, as the ragged edges will help the patch grip the surface.

Examples of an environmental repair would be the repair of a truck roof to keep out rain, dust or NBC contamination. A hull repair on a Bradley fighting vehicle to stop water entering through a hole below water line while fording a river or stream. A shipping container to keep out rain and dust. A windshield repair on a HUMMV or truck to keep the windshield intact. Or a combination of any of the above.

A quick environmental repair can be accomplished by cleaning the area as well as possible, and removing all the dust, dirt, water and oil. The light curing putty is then used to fill the hole, crack, or tear, and then exposed to sunlight or a UVA lamp. For larger holes, the damaged area should be patched with the fiberglass patch after using the putty to impart good wetout and adhesion of the patch to the damaged surface. An environmental patch is only meant to last for a short time until a more a more complete patch can be made.

If extra time is available a more permanent structural repair should be made to the damaged surface.

STRUCTURAL REPAIR:

A structural repair takes more time to restore the surface to its original strength.
Structural repairs are meant to restore most or all of the structural integrity of a part or structure.

Examples of structural repairs would be repairing pipes or ducts which are pressurized. Repair to a HUMMV hood, sides, roof or floors. Repairs to water or fuel tanks to stop leaks. Repairs to structural metal parts when a welder is not available. Repairs to canopies and skins of helicopters. Skid plates which have worn through. Any hole through armor plates to help restore its integrity.
Structural repairs are more permanent than environmental repairs and should be treated as such.

The area to be repaired should be thoroughly cleaned and sanded if possible. Putty should be applied prior to the patch, if the surface is pitted or very rough. The patch is applied being very careful to work out as much of the air between and under the laminates as possible. The best patches will have no air in the laminates.

Patches surrounding a part such as a pipe should be lapped over themselves for best results. **(Fig 2)**

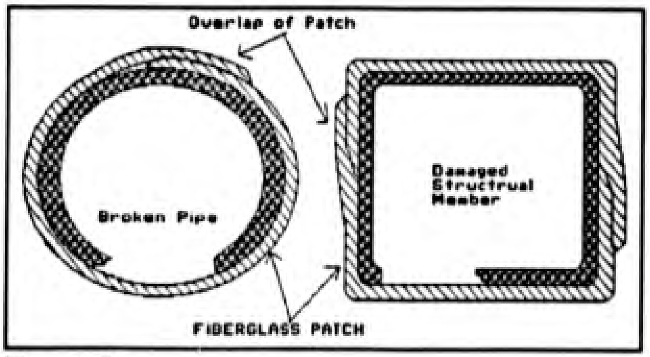


Figure 2

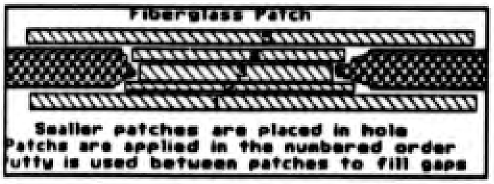


Figure 3

Patches over large surface areas or covering large holes should be applied from both sides of the repair. **(Fig. 3)**

The best bonding occurs when the area to be patched is fully wet out with resin/putty and there are no dry spots. All of the excess resin/putty should be squeezed out of the repair area. The strength of a patch is from the fiberglass, not the resin. The bonding is controlled by the resin distribution under the patch and the bond achieved to the damaged part. The bonding resin should be as thin as possible and still cover the area.

GENERAL PROCEDURES:

IT IS IMPORTANT TO REMEMBER THAT THE CLEANER THE SURFACE TO BE PATCHED THE BETTER THE PATCH WILL BOND.

Proper application procedures are as follows:

Shade area to be patched if possible.
Clean the area to be patched. Remove all oil or moisture.
Sand or scuff up the surface where the patch is to be applied
If necessary, apply putty just prior to adding patch (do not cure).
Remove patch from pouch and remove clear bottom film.
Apply patch with top Yellow film up.
Work patch around contours on part over putty if used.
Press out all air bubbles and excess resin.
Move part into direct sunlight or expose to UVA light source,
Remove Yellow film being careful not to lift patch from surface. (patch will not cure until Yellow film is removed).
Expose to light source for 5-10 minutes until patch is hard.
Remove top clear plastic film.
Repeat process if additional plies are necessary.

For pipes or other objects that are to be surrounded by patch, the plastic film must be removed in all areas where the patch overlaps itself. The patch will not stick to the clear plastic film.

If in doubt as to whether the patch is strong enough, add more layers.

2.8. Field Testing of Field Repair Patch, Government Utilization (Phase III), and Final Report.

2.8.1. Approach.

Originally the Program called for the manufacture and field trials on three different sets of patches for FRP, steel and aluminum surfaces. Near the end of the program, it was determined that the use of the putty plus the patch would give satisfactory bonding against steel, FRP, and aluminum. Therefore, only one set of 150 patches incorporating the putty pouch were submitted as the final deliverables. However, the initial patches were sent to TACOM and to the U.S.Army Materials Technology Laboratory (Watertown, MA) for comment and initial feedback. Several outside demonstrations were held in 1991 to show other groups actual field type repairs with the patch in order to elicit feedback and gain direction as to modifications. The speed and the completeness of the cure impressed all groups.

With the delivery of the final patch system, Sunrez also requested and finally received a NSN number from TACOM to enable direct ordering from any U.S.Government Agency. Commercial putty and repair systems are now also being pursued as the putty and patches have reached a commercial level (Phase III of the SBIR Program).

2.8.2. Results.

Sunrez shipped 1055 patches and 1055 tubes of sunlight cured putty within two weeks of receiving order from TACOM on January 19, 1991 for Desert Storm. Most of this order was laid up and packaged by hand. This effort to start up the initial commercial patch and putty manufacture forced the development of the initial manufacturing processes.

Sunrez demonstrated the field repair patch system at the U.S.Army Materials Technology Laboratory on July 15, 1991 incorporating the final configuration of the patch, putty, and lamp. (William Haskell coordinated this activity at AMTL, Watertown. A demonstration was also given at Wright Paterson Air Force Technology Laboratories in Dayton, OH on July 16, 1991. (Ted Reinhart coordinated this activity.) In addition, a demonstration was held in the Washington, D.C. area June 24-26 as part of AMC/CASCOM " Supporting the Battlefield of the Future"(Logistics Research Day).

Commercially, Sunrez light cure resins are being seriously evaluated by the three largest boat manufacturers in the U.S. at their Florida manufacturing plants. Our putties are now commercial in Texas and in southern California through small distributors. Sunrez received a Certificate of Recognition from the United States Army Materiel Command for the Sunrez response in sending field repair patches and putty for Desert Storm. A copy of this letter accompanies this report in the Appendix.

3.0. DOCUMENTATION.

The source of the information utilized in the discussion has been taken from monthly reports #1 through # 22 for this program (DAAK04-89-C-0019) starting November 5, 1989 through January 20, 1992. The Final Report, Phase I. Field Repair of Composite Lightweight Armor (Contract # DAAL04-87-0062) dated May 14, 1988 from the initial SBIR Phase I program and the Sunrez Corporation proposal for the Phase II SBIR program were also utilized as a references to the work reported in this present report.

The monthly reports, this final report and the resulting patches and photolamps constituted the deliverables under this program. No other document source was utilized in the preparation of this report.

4.0. STATUS OF ACCOMPLISHMENTS.

All tasks assigned in the contract statement of work were completed successfully and on time.

The actual items or tasks assigned with the resultant accomplishments are listed.

1. Develop the Fastest Sunlight Curing Resin Which Also Has Outstanding Physical Properties.

Several very fast UV$_a$(sunlight) cured resins and formulated resins were developed and exceed the original goal of about a three minute cure in sunlight. The cure rate achieved for 0.25-inch fiberglass prepregs or patches was about 2-3 minutes which is less than half the time found in Phase I program and far faster then any related system now known. The physical properties of the prepreg are outstanding. The tensile strength of the best resin cured, an acrylated epoxy novolac, was over 11,000 psi with good elongation. The vapor pressure of the selected resin system has been reduced.

2) Maintain or Improve the Ballistic Performance of the Resin Formulations.

The faster resin systems also had the high tensiles(>11,000 psi) and good elongation (>3%) required for better ballistic performance. Panels were only tested ballistically in Phase I of this program which demonstratd that these light cured resins performed very well compared to conventional resins. The achievement of the same or better properties in the Phase II program demonstrates that the ballistic properties should be very good.

3) Develop Improved Reinforcement Systems.

The use of higher strength fiber glass such as R glass woven roving can give the maximum composite performance. The high performance achieved with standard E glass with clear sizing gave a very satisfactory patch which cured in >0.25-inch thickness without incurring the significant cost of the R glass. It was not necessay to try to utilize Kevlar. S-glass would work if available with a clear sizing.

4) Develop Field Repair Patch for Various Composite and Armor Systems.

A field repair patch complete with an attached pouch for putty has been developed and field tested. This patch can be made in dimensions from 6" x 6" up to 36" x 36" and cured in sunlight in 2-3 minutes or with a handheld UV lamp working off of a vehicle battery. The one part patch has a shelf life at room temperature of about 12 months and is easy to use. A transparent UV$_a$ blocking film covers the patch while it is being worked into place and then is removed. The repair can be built up in stages by successive layers of patch. The patch will adhere to most common surfaces to be found on military vehicles such as urethane paint, steel, alumminum, and FRP if clean. When the putty is used, only one patch is needed for all of the surfaces noted. The use of the putty included in the kit for the initial surface preparation ensures that there is sufficient wet out and filling of uneven surfaces to maximize the bonding of the patch. The cure time, the physical properties, the general utility for all surfaces, the compact nature, the low cost, and ease of use exceeded all goals set for this repair patch system.

5) Develop Portable UV$_a$ Lamp.

The portable UV$_a$ photolamp was designed and built. The lamp was based on a mercury vapor lamp and is commercially available. The electronics of the device were combined into one three pound package including the ballast, inverter, transformer. The whole unit including a 20-ft cord weighed under six pounds. The unit works off of a 24-V U.S. Army vehicle battery and cuts off when the battery has less than 21-V power. The cost of this solid state system would probably be less than $300 in volume. Ten of these lights were sent to the U.S. Army Materials Technology Laboratory to complete the program. All goals were exceeded on this task.

6) Develop Field Repair Techniques Utilizing the Field Repair Patch and Putty.

The use of the patch has been simplified to approximate that of a Bandaid^{r}. The use of the putty removes a great deal of uncertainty regarding the proper surface treatment. An outline of simple directions has been included on the package. A description and procedures for the general field repair techniques available with the Sunrez Field Repair Patch has been included in this report. These procedures are based upon techniques which have been proven out with the Sunrez light cured resins and experience drawn from commercial practice used in the boat fabrication area.

7) Design and Produce Field Repair Patches and Putty for Field Trials. Maintain Appropriate Reporting and Issue Final Report.

Over a 1000 field repair patches and 6000 tubes of the putty were deployed during the Desert Storm Operation. A final patch configuration has been established and is available for order through an NSN number. A commercial process for producing these patches has been developed. This work has all been documented throught issue of 22 monthly reports and the issuance of this Final Report.

5.0. LABORATORY RESULTS/TESTS.

Laboratory tests and results have been reported monthly in the 22 Program Monthly Reports. These results have been summarized in detail in this Report in Section 2.0 under Results. Additional testing was performed under field conditions with over one thousand patches submitted to Desert Storm. Additional patches were submitted to TACOM and U.S.Army Materials Technology Laboratory for their evaluation. Demonstrations were held for the Composite Repair Group at Wright Paterson Air Force Base. The testing went very well and all comments and suggestions were incorporated into the patch and putty. The key results are that the patch cured within two to four minutes in sunlight and had good adhesion and physical properties, and could be stored for 12 months on the shelf. These results were achieved.

6.0. SUMMARY.

The successful development of the field repair patch and the completion of this Phase II SBIR Program depended on achieving several technical goals. (The results of the Phase I Program had demonstrated the feasibility of achieving many of these goals with this one part light cured system.)

The most important technical goal was the development of a fast UV_a photocure resin which produced good physical properties. This was accomplished by evaluating the rate of cure for a large number of commercial and development resins and base stocks. The optimum resin was found to be an acrylated epoxy novolac although other vinyl esters would be satisfactory. This optimum resin (with several backup resins) was then compounded or formulated with a large number of different monomers including styrene, acrylate esters, methacrylate esters, vinyl toluene, various cross linking oligomers. It was found that the use of only 20% of a monomer mixture consisting of vinyl toluene and hydroxypropyl methacrylate gave very rapid cures and minimized the volatiles or emissions.

This resin formulation was incorporated into an alternating stack of E-glass fabric consisting of 24-oz. woven roving, mat, 24-oz. woven roving, and finally mat. This patch was 0.25-inches thick and cured in sunlight in about three minutes. The glass had to have a clear sizing for the best cure results. The adhesion of this patch to fiberglass resin and aluminum surfaces was satisfactory. However, it was sometimes difficult to guarantee that the surface/patch interface had sufficient resin for good wet out or had been prepared well enough. Optimization of the adhesion to steel was the most difficult aspect of the adhesion improvement and required the use of primers. Finally it was found that the most dependable method was to use a light cured putty to cover the surface initially, and then apply the patch to this wetted out out surface. The putty was based on a unsaturated polyester with a small amount of a trimethoxy aminosilane added along with a small amount of a thickener such as fumed silica. This combination produce good dependable adhesion to aluminum, steel, and fiber glass reinforced resin surfaces. One hundred and fifty patches were sent to the U.S.Army Materials Technology Laboratory (Watertown, MA).

Stability tests at 140°F showed that 0.1% hydroquinone addition gave at least six months shelf life under nominal desert conditions, and this should be good for at least 12 months storage under normal conditions. The rate of cure is slowed somewhat, but it is still satisfactory.

The TACOM order for over a thousand patches and thousand tubes of putty for Desert Storm forced a rapid development of a process to make commercial quantities of the patch. This process consisted the impregnation of the stacked/stitched fiber glass fabric with a gentle rolling motion followed by degassing. The stack is then cut to size and wrapped with PVA release film. The transparent UV_a film is then placed on one side and this completed patch sealed into an aluminum pouch, ready for shipment.

In order to cure the patch inside vehicles or at night, a compact light weight photolamp was developed that operated off the standard U.S.Army 24-V vehicle battery. This unit consisted of a 100-watt mercury vapor bulb, standard commercial housing socket, a custom designed combined solid state ballast, inverter, and transformer. The whole unit weighed less than six pounds and can cure a 10"x10" patch in five minutes. Ten prototype units were sent to the U.S.Army Materials Technology Laboratory(Watertown, MA). This patch has been assigned NSN number 8040-01-346-1339 by TACOM, and it is to be incorporated in their Battlefield Damage Repair(BDR) Kit.

7.0. CONCLUSION.

A practical storable field repair patch for composites, armor, and other equipment has been developed which cures rapidly in sunlight or with a portable UV lamp which works off of U.S.Army vehicle batteries. This is a one-part resin system. The physical properties and cure rate exceeded all goals. This patch has already been field tested in Desert Storm and has demonstrated that it is practical for the repair of any type of field repair of damaged vehicles, composite or metal structures and other items.

8.0. RECOMMENDATIONS.

The light cured resins developed for this field repair patch not only cure rapidly, but with outstanding physical properties. Sunrez recommends that these same or similar resins be utilized for structural applications requiring fiber glass systems. The U. S. Army is planning on increasing the composite content of vehicles and armor in order to reduce the weight and increase the mobility of its fighting equipment. The use of these light cured resins can offer fabrication techniques and procedures which can lower the overall cost of this increase of composite content and vehicle modification. Sunrez recommends that a development program be initiated which determines the cost and property advantages of fabricating composite structures utilizing these light cured resins.

Light cured resins can form the basis for other repair systems in addition to the field repair system already developed for the U.S.Army. For instance, this system could be used for the the repair of aircraft canopies, possibly fuel tanks, and the repair of other special structures or parts. Sunrez recommends that other repair problems be considered for this resin system. Sunrez is prepared to work with those having the problem repair in order to solve it. It would be very useful to conduct field demonstrations of the repair system or even to put together a video tape to demonstrate the practical repair techniques that are possible with the field repair patch and putty. Deployment of this patch is the best recommendation that we have as far as improvements in its effectiveness are concerned since we believe that this program has resulted in a completely successful field repair patch.

APPENDIX

DEPARTMENT OF THE ARMY
HEADQUARTERS, U.S. ARMY LABORATORY COMMAND
2800 POWDER MILL RD., ADELPHI, MD 20783-1145

REPLY TO
ATTENTION OF

June 19, 1991

Corporate Technology

Mr. Mark A. Livesay, President
SUNREZ Corporation
1374 Merritt Drive
El Cajon, California 92020

Dear Mr. Livesay:

Now that Operation Desert Storm is behind us, I wish to take this opportunity to commend SUNREZ Corporation for your outstanding performance in the development of the U.V.-cured composite patch kit.

It is dedication such as yours that provided our soldiers with the very best that our nation can provide.

Your exceptional response in gearing up production of the kits and in support of the United States Army is greatly appreciated. You have earned our admiration and confidence. Congratulations for a job well done and keep up the good work!

A Certificate of Recognition for SUNREZ Corporation is enclosed.

Sincerely,

Great job!

Jerry C. Harrison
Major General, U.S. Army
Commanding

Enclosure

United States Army Materiel Command

Certificate of Recognition

awarded to

Sunrez Corporation

For

Outstanding Cooperation and Exceptional Response
to U.S. Army Requirements in Support of
Operation Desert Shield/Desert Storm

WILLIAM G. T. TUTTLE, JR.
General, USA

AMC FORM 1616

DETAILED EXPERIMENTAL RESULTS

A.2.2. Resin Cure rate and Physical Properties Optimization

Initial Setup and Results. Since the primary focus of this program was on the rate of photocure, the results of Phase I based on several commercial resins were reviewed. Alternatively, the more rapid cure rate resin could be utilized in a thicker patch curing in a slower but acceptable time. A large number of unsaturated polyesters and vinyl ester resins were requested from about ten producers. We knew that our photocure system based on the Palatal photoinitiator gave equivalent or slightly better properties than the same resin which had been cured conventionally with peroxide. Therefore the commercial technical data bulletins offered a guide as to the properties expected. However, the rate of photocure had to be empirically determined. These resins represented a survey as to what was available and would offer leads as to what type photocurable resins would give the most rapid cure rate while maintaining good properties. Some of the more important criteria for rapid photocuring of these resins were that they had to have low color (Gardener less than 4), relatively low inhibitor level, and non-promoted (no cobalt or amine). In addition, a number of various monomers were requested at this time.

In the initial photocure screening results of the first resins which we received, the cure rates were much faster with the vinyl ester resins. The technical data bulletins also indicated that the vinyl ester resins had tensile strengths above 10,500 psi, which placed them as group 10-15% higher than the unsaturated polyester resins. In addition, the vinyl esters also had a higher T_g and usually higher elongation than the unsaturated polyesters. We decided to focus on the vinyl ester resins while continuing to check on various commercial unsaturated polyester resins that we received so as not to overlook any obviously good resins. Information on these other resins was useful in the formulation of a rapid cure putty which was planned to compliment the repair patch.

Commercially available vinyl ester resins usually consist of a base stock oligomer which is either an acrylated or methacrylated epoxy bisphenol A resin with a functionality of two. This base stock was diluted to the proper viscosity with 30-45% styrene and then the inhibitors and optional promoters may be added. In order to screen the vinyl ester resins, a selection of the various types available were evaluated in the course of the program.

At the start of this program, the only commercial resins which were available contained 30-45% styrene. In order to run a preliminary screening of the effect of various mono and polyfunctional monomers, these monomers were added to lower styrene(35%) vinyl resins in 10-20% amounts. The effects that were desired were more rapid cure rate, and reduction of surface tack when cured in the presence of air. Initially, we believed that air may be slowing down the cure rate since it inhibited the surface cure.

The initial vinyl ester type resins and monomers that were screened with different levels of the photoinitiator were:

Base Backbone Resin	Monomers
bisphenol A diacrylate	methyl acrylate
bisphenol A dimethacrylate	methyl methacrylate
diacrylated bisphenol A	styrene
dimethacrylated bisphenol A	dimethylaminoethyl acrylate
triacrylated novolac	dimethylaminoethyl methacrylate
trimethacrylated novolac	diallyl phthalate
	vinyl pyrrolidone

Other considerations with respect to resin properties were adhesion and fire resistance (not required in this program).

A standardized procedure was developed and used for quantitatively measuring the rate of cure so that an accurate comparison for the rate of cure was obtained. It was assumed that the rate of cure was directly measured to the time necessary to achieve the maximum temperature during cure. Although the photolamp contributed to the temperature rise the peak exotherm was usually rapid and reproducible. The actual peak temperature was indicative of the amount of monomer present.

Standardized Procedure for Measuring Time to Maximum Curing Temperature(and Maximum Reaction Temperature)

A 25 gram sample of the monomer or resin was weighed out into an aluminum weighing dish, 0.25 inches deep and then mixed with 0.4 to 0.8% of the photoinitiator(L PALATAL X999 1-02Z, BASF). The photoinitiator was thoroughly mixed with the sample and the resin allowed to settle to a flat surface. The aluminum dish was placed on a glass plate situated directly under an UV lamp (Uvaspot 400 watts) which was 12 inches from the surface of the resin in the weighing dish. The UV lamp was already on and at steady state. As soon as the dish of resin was placed under the lamp, a thermal couple was inserted into the resin and this becomes time equal to zero. The temperature is plotted against time. An example of such a temperature/time plot was given in Figure 2. The time to reach the maximum reaction temperature is noted along with the maximum temperature reached. When relevant, the Barcol and the nature of the cured disc is described.

As a reference point, several commercial vinyl ester resins were run and are listed in Table 1. Initially, several blends were made from bisphenol A diacrylate (Ebecryl 150) and 30% by weight of various monomers and these were also photocured. This permitted a brief determination of the assumption that curing would result with our own internally blended vinyl ester resins. These resins did cure satisfactorily and were then run under the standard conditions. This was important to our goal of being able to identify the key components that were necessary to make a resin which cures at the optimum rate, and then actually blending those components and achieving the predicted result.

The cured resin samples were examined for surface tack and extent of cure. In all of these cases the surface was tacky as expected without a plastic film being added to the surface to keep out the air which causes inhibition of surface cure. With the transparent plastic film, the surface rapidly cures hard. Most of these photocured commercial resins had a Barcol hardness 10-30% higher than the corresponding Barcol given by the manufacturer for a peroxide cure. Dow reports typical Barcols for Derakane 470-36 as 40 while those for the 411-35 as 35, while we experienced Barcols of 45-55 and 45 respectively. (These Barcols were measured from the backside which is protected from the air during cure, and therefore the surface was not tacky due to air inhibition.) Since we were running our standard photocure evaluation adiabatically, we did get significant warpage of the resin "plate" or disk. In order to do a Barcol, it was necessary to have a flat, smooth surface, which was not always available on the cured resin discs.

A number of important factors came out of this initial work to establish baseline conditions:

1). There is an optimum amount of photoinitiator for each resin which is a function of the resin, the thickness of the layer to be cured, the level of color of the resin (light or dark), the chemical nature of the monomer and the multifunctional backbone molecule. Most of the resins had a maximum in rate within the range of 0.4-0.6% added photoinitiator, and then showed a slowing in rate with increased levels of photoinitiator. The excess photoinitiator after causing the upper layer of resin to cure may then effectively screen out much of the UV light from the uncured layers below the top layer. The darker the resin the more serious was this effect since there is significant absorption of the light by the resin already. For instance Derakane 470-36 cured very well through most of the plate, but the bottom was still wet due to the high color of this resin.

2). Although the first four commercial resins in Table 1 are similar, there was a variation of 30% in the rate of cure at the 0.6% photoinitiator level for instance. The increased amount of styrene monomer or differences in inhibitor level can explain the increased reactivity of 411-45 over 411-35.

3). A FR resin containing brominated resin was successfully cured which indicates that standard FR vinyl ester resins can be used as they come from the manufacturer. No antimony oxide was used in these formulations.

4). The fastest commercial vinyl ester resin that we found in this initial screening of commercial resins was based on a methacrylated novolac (Derakane 470-36) which is approximately a trifunctional backbone molecule. The color of this resin was significantly darker than the normal vinyl esters. The Barcol was 45-55 (Dow reports a Barcol of 40 with a tensile about 11,000 psi). This resin was recommended for service above 300°F. Since three methacrylate groups were available to crosslink from each molecule instead of two as found in the bisphenol A derived methacrylates such as Derakane 411-35, reactivity was considered to be at least 50% faster. This pointed out that the higher the number of polymerizable functional groups on the molecule, the faster the overall cure of the system. We determined that if we could obtain or produce a clearer acrylated or methacrylated novolac type resin, we should be able to obtain significant depth of cure due to the predicted high rate of cure.

5. The preliminary evaluation of the effect of blending monomers with the bisphenol A diacrylate showed that comparable results can be achieved with similar commercial systems when we know what they contain. Comparison of Derakane 411-35 with 0.4% photoinitiator (run #10) with run # 28 which was a similar blend gave a time to T_{max} of 10.3 versus 11.3 which was close.

These initial trials were meant only to establish a baseline for the matrix evaluation of the available resins, but led directly to some significant factors for improving the rate of photocure:

* The backbone monomer preferably should be a multifunctional material such as a novolac based vinyl ester.

* The photoinitiator must be optimized for each formulation and thickness to be run.

* The evaluation results appeared to be extrapolatable to forming new fast curing resin formulations.

* Higher monomer concentration will improve the rate of cure. (Higher monomer concentration may negatively affect some the physical properties depending on the situation.)

* Acrylate and methacrylate monomers are faster than styrene.

TABLE 1
PHOTOCURE RATES FOR VARIOUS VINYL ESTER RESINS

Resin/Material	%Initiator	Time to T_{max} min	T_{max}, °F	Comments
1. Koppers NP9200	0.4	8.5	225	slight surface tack
2.	0.6	6.8	256	"
3.	0.8	8.4	223	"
4. Koppers NP9300	0.4	6.6	228	slight surface tack
5.	0.6	6.2	256	"
6.	0.8	7.0	258	"
7. Hetron NP	0.4	6.5	256	"
8.	0.6	6.1	282	"
9.	0.8	6.4	281	"
10. Derakane 411-35	0.4	10.4	178	"
11.	0.6	8.7	170	"
12.	0.8	9.7	172	"
13. Derakane 411-45	0.4	6.4	268	"
14.	0.6	6.8	273	"
15.	0.8	6.5	298	"
16.	1.2	6.9	228	"
17. Derakane 470-36 (novalac resin)	0.4	2.4	228	bottom liquid
18.	0.6	2.3	223	"
19.	0.8	3.6	223	"
20. Derakane 510A	0.4	5.3	273	slight surface tack
21.	0.6	5.5	267	"
22.	0.8	5.5	290	"
23. Derakane 8084	0.4	11.0	228	surface tacky
24.	0.8	10.5	198	"

TABLE 1 (CON'T)

The resins for the following runs are mixtures of Bis phenol A diacrylate and 30% various monomers with 0.4% photoinitiator.

25. Dimethylaminoethyl methacrylate	cured
26. Dimethylaminoethyl acrylate	cured
27. Dimethyl maleate	cured
28. Styrene	cured

A significant difference was found between two acrylated base stocks containing no monomer. In Table 2, Run 2 was at least twice as fast as the acrylated material in Run 1. (Note that acrylated resins usually photocure faster than methacrylated ones.) Run 1 had a time to T_{max} of 12 minutes which is as long as any of the commercial vinyl esters with a loading of 0.4% photoinitiator. On the other hand, the material in Run 2 had a time to T_{max} of 4.6 which was faster than any of the commercial resins with a bisphenol A backbone. The only differences between these two resins were that there was more color in the slower one(Run 1) and that chemically Run 1 represents a bisphenol A diacrylate while Run 2 was more like a standard acrylated epoxy vinyl ester. Other higher molecular weight acrylated species were also run for comparison and gave even faster reaction times than Run 2. The Gardener color of the acrylated epoxy, the urethane diacrylate, and the polyester were 1, 1, and 3 respectively. The color of the slower acrylated bisphenol A was 6. Although color was detrimental, the rate of cure was also dependent on the chemistry of the particular acrylated monomer or backbone.

The trifunctional acrylates which are used as crosslinking materials and reactive diluents to lower viscosities were very fast as shown in Table 2. These materials are nearly colorless or even water white and lower viscosity. More importantly the presence of more than two reactive acrylate (or methacrylate) groups in one molecule was one common denominator that appeared to make these materials so reactive. The highly reactive (but significantly colored) Derakane 470-36 also had a time to T_{max} under three minutes (2.4 min. with 0.4% loading), and it has about three reactive acrylate groups per molecule. In Table 2, both the pentaerythritol tetraacrylate (Run 12) with 4 groups and the TMP (Run 13) with three groups were the fastest photocure materials found at this point of the program. The Barcol hardness on some of these fast photopolymerized acrylates went above 60.

The results with the pure monofunctional monomers were not impressive. The only such monomer in these initial evaluations which homopolymerized with 0.4% photoinitiator was hydroxypropyl acrylate. However, it was very fast. Although styrene did not polymerize with the photoinitiator alone, it is a highly reactive diluent/ reactant in the vinyl ester resins. Most of these monomers even if they did not photocure by themselves, would cure in the presence of a base stock as in the commercial resins. (Evidently when the photoinitiation of the vinyl ester resin starts, it starts from the methacrylated or acrylated epoxy bisphenol A molecule and the subsequent radical which forms is reactive toward styrene.)

TABLE 2
PHOTOCURE RATES FOR VARIOUS VINYL ESTER RESIN COMPONENTS
(standard procedure)

	Resin/Material	% Initiator	Minutes Time to T_{max}	T_{max}, °F	Comments
1.	Bisphenol A diacrylate (Ebecryl 150)	0.4	12.0	172	
2.	Acrylated epoxy (Ebecryl 600)	0.4	4.6	207	hard to mix
3.	Urethane diacrylate (Ebecryl 284)	0.4	2.3	208	hard to mix
4.	Polyester diacrylate (Ebecryl 584)	0.4	2.1	220	hard to mix
	Pure Monomers				
5.	Styrene	0.4	no apparent polymerization		
6.	Dimethyl Maleate	0.4	"		
7.	Diethyl Fumarate	0.4	"		
8.	Dimethylaminoethyl Acrylate	0.4	"		
9.	Dimethylaminoethyl Methacrylate	0.4	"		
10.	Hydroxypropyl Acrylate	0.4	1.6	368	very fast
11.	Styrene / Diethyl Fumarate	0.4	no apparent reaction		

TABLE 2 (CON'T) Multifunctional Monomers

12. Pentaerythritol Tetraacrylate	0.4	1.0	447 very fast
13. Trimethylol propane triacrylate (Sartomer 351)	0.4	0.7	410 very fast
14. Trifunctional Triacrylate (Sartomer 9012)	0.4	2.1	363
15. Trifunctional Trimethacrylate (Sartomer 9011)	0.4	2.1	275

Cure Rate as a Function of Chemical Structure and Monomer. In Table 3 are listed the T_{max} or cure rate of a number of fast resins which represented a continuing effort throughout this program of continuing evaluation of new resins and ideas for improving the cure rate of the basic resin system to be selected for the field repair patch. After obtaining these more rapid cure rates, tensile strength and other physical properties were addressed as criteria for selection of the desired resin.

Some of the runs listed in Table 3 were reruns of previously evaluated resins to ensure reproducibility. These results were reproducible to within 10% on the Time to T_{max} and 15% for T_{max}.

Comparison of the cure rates for the various bisphenol A (BPA) type structures in Table 3 showed that the slowest rates (Time to T_{max}) were found for BPA which is directly acrylated without an ethoxy or epoxy group insulating the acrylate ester from the aromatic BPA ring, E-150. The addition of various monomers did not help and the resulting polymers were not satisfactory. On the other hand, an acrylated epoxy BPA (E-600) was very fast with and without various monomers including styrene. The acrylated ethoxy BPA (S-349 and S-348) was almost as fast as the acrylated epoxy BPA compounds. E-600 with 30 % styrene should be chemically very close to the current vinyl ester resins such as Derakane 411-45 or Koppers 9200NP, yet it peaked in 2 minutes while the commercial resins were about 7 minutes. The amount of inhibitor was about the same in these materials so that the explanation must lie in the light colors achieved with the E-600 and related materials from Sartomer and Radcure and from others who are making these materials for standard photocure systems in the electronics industry. The increased color of the large scale commercial vinyl resins comes from the catalysts employed for the methacrylation or acrylation of the epoxides. Although many of these commercial resins worked well(Derakane 411-45, Koppers 9200NP), several of the lighter related resins from Sartomer and Radcure photocured in half the time, 2 to 4 minutes.

From these program results, we next focused on trying to obtain the fast curing novolacs which were lighter in color than Derakane 470-36. We evaluated E-629, which cured faster and more completely.

Several paired examples of methacrylate versus acrylate were run and are listed in Table 3. There was no question a pure methacrylate ester system might take two or three times longer than an acrylate system. However, the physical properties of the methacrylate system appeared to somewhat better with respect to Barcol and elimination of surface tack.

TABLE 3
PHOTOCURE RATES FOR VARIOUS VINYL ESTER RESIN COMPONENTS

Resin/Material	% Initiator	Minutes Time to T_{max}	T_{max}, °F	Barcol	Comments
1. Bisphenol A diacrylate (Ebecryl 150)	0.4	7.5 7.8	131 126	wet wet	soft
2. E-150 plus 30% dimethylaminoethyl acrylate	0.4	7.3	115	-	very soft
3. E-150 plus 30% N-vinyl-2-pyrrolidone	0.4	5.1	226	14	soft
4. E-150 plus 30% dimethylamino methacrylate	0.4	5.5	142	-	very soft
5. E-150 plus styrene ran twice	0.4	12.1	215		wet sticky
6. E-600 epoxy BPA diacrylate plus 30% styrene	(0.4%) (0.2%)	1.9 2.4	249 267		wet wet
7. E-600 plus 25% hydroxypropyl acrylate	(0.2%)	1.9	254		
8. E-600 plus 25% dimethyl fumarate	(0.2%)	3.0	174		
9. E-629 epoxy novalac diacrylate plus 30% styrene		3.0	263		wet
Pure Monomers and Components (0.4% initiator)					
10. Hydroxypropyl methacrylate		3.5	277	45	dry
12. Hydroxypropyl acrylate (repeat)		1.0	275	-	sticky

TABLE 3 (CON'T)

13. Hydroxyethyl acrylate	0.8	363	-	sticky
14. Hydroxyethyl methacrylate	3.2	298	44	dry
15. Trimethylolpropane triacrylate (S-351) (repeat)	1.2	308	-	very brittle
16. Trimethylolpropane trimethacrylate (S-350)	2.5	238	58	dry/brittle
17. N-Vinyl-2-pyrrolidone	8.4	226	no polymer	
18. Diallyl phthalate	no reaction			
19. Methyl methacrylate	no reaction			surprising
20. Ethoxylated BPA (0.6%)	2.2	188	38	sl.wet
diacrylate (S-349) (0.4%)	2.6	224	32	sl.wet
21. Ethoxylated BPA dimethacrylate(S-348)	2.8	169	45	"
22a. 1,4-Butanediol diacrylate (S-213) 0.4%	1.1	>400		very brittle
b. S-213 plus 0.2% initiator	1.0	>400		"
c. S-213 plus 0.1% initiator	1.3	>400		"
23.1,4-butanediol dimethacrylate (S-214)	2.8	252		brittle
24. Tripropylene glycol diacrylate	1.8	348		very brittle
25. BPA epoxy dimethacrylate(0.6%)	3.5	230	42	sticky
E-1608 (0.4%)	4.1 22	219	38	sticky
26. BPA epoxy dimethacrylate(0.4%)	7.4	188	54	sticky
E-616 (0.6%)	5.4	177	50	sticky
27. Epoxy novolac acrylate (0.4%)	2.6	255	50	sticky
E-629 (0.6%)	2.3	190	52	sticky
28. BPA epoxy diacrylate (0.4%)	7.1	153		
E-3700 (0.6%)	6.3	165		

The evaluation of possible additives to increase cure rates and hardness is listed in Table 4 which included the use of various commercial photoinitiators and known light absorbing compounds in the UV$_a$ and visible light range. No additive seemed to speed up the reaction with the photoinitiator and only benzyldimethylketal might have had a slight effect with 470-36 at the 0.2% level. This effort was discontinued because the apparent lack of promise.

TABLE 4
EVALUATION OF ADDITIVES

(Also checked with Derakane 411-45 and 570-A with the same equivalent results)

	Time to T$_{max}$	T$_{max}$, °F	Barcol	Comments
Derakane 470-36 plus 0.2% benzyldimethylketal	3.1	178	56	
plus Darocur 4043	no polymerization			
plus fluoranthene	no polymerization			
plus acenaphthene	5.1	189	----	
plus Irgacure 184 (0.4%)	4.8	141	48	
(0.2%)	3.4	191	45	
plus Irgacure 907	4.3	153	50	
plus Irgacure 500	5.2	157	45	
Derakane 411-45 plus Irgacure 651	6.7	177	42	
plus benzyldimethyl ketal	7.9	190	42	
plus camphorquinone	6.3	188	35	
plus Darocur 1664	no polymerization			
plus Darocur 1173	8.0	205	40	
plus Irgacure 651	6.2	194	40	
plus Irgacure 907	10.1	222	40	

Formulation Work and Continued Evaluations. The better candidate base stock and blended commercial resins were blended with various monomers as listed in Table 5. These better candidate resins included novolacs such as Ebecryl 629(Radcure), and commercial low color, low inhibited BPA epoxy resins such as Dion Ver 31351 (Reichhold), and DER 411-45 (Dow). The novolacs photocured in our testing in four minutes or less, had Barcols of >50, higher tensile strengths, and higher heat deflection temperatures. The disadvantage with the novolacs was to obtain one with sufficiently light color and low inhibitor level to permit thicker section curing. One resin in this evaluation series was VE 8730-34 (Interplastic) which cured dry immediately and had outstanding physical properties including high heat deflection, 320°F. This resin was considered a backup resin at this point of the program for the final candidate resin.

As a check on the effect of photocuring on the physical properties, several good commercial resins were photocured and the tensile tests were run and compared with the literature values for the cured resins obtained with peroxide cure. The testing of tensile strengths on photocured VER 31351(old Koppers 9200-NP was advertised to be 11,800 psi with peroxide cure) gave a high value of 11,400 psi (with an average of six tests of 10,900 psi)with no post cure. DER 411-45 is advertised to have a tensile of 10-11,000 psi with peroxide cure. Photocured DER 411-45 tested to 10,100 psi, (the highest of three tests with the average of 9,500 psi). These tensile test results showed that the photocured resins gave tensile strengths that are well within the manufacturers guidelines for the conventionally cured resin. Single bars of several other resins were tested and found to be within the manufacturers guidelines for the conventionally cured resin. These results showed that the published tensile strengths for the commercial resins are a valid guide for evaluating the expected tensile strength of a given photocured resin.

Tensile strengths were performed as needed, but the focus on physical properties shifted to adhesion strength (lap shear), since the adhesion of the repair patch to the damaged part is one of the important factors in the design of the resin system. It was now possible in the program to expand our evaluations since there were a number of good candidate resins and good guidelines for selecting resins and resin mixtures.

We were not concerned about reductions in tensile strength resulting from resin modifications to improve adhesion if the change in tensile was only of the order of 10-15%. The major strength in the patch is derived from the glass reinforcement, and the resin acts as a binder and to distribute the load within the reinforcement. Industry data shows that the type of reinforcement has more to do with the specific strengths of a given composite than the tensile strength of the resin matrix within limits.

The addition of various candidate monomers to both 31351 and 629 resins showed that the acrylate monomers helped to speed up the vinyl novolac and the BPA epoxy vinyl ester resin somewhat. No real advantage for these monomers over styrene was found except for some increase in speed and lower volatility. The following monomers appeared to work the best for diluting or modifying the novolac or other selected base stock resins: hydroxypropyl acrylate, divinyl benzene, 1,4-butanediol diacrylate, and styrene as the diluting monomers for the base resins. These results are listed in Table 5.

TABLE 5
PHOTOCURE RATES FOR VARIOUS VINYL ESTER RESIN COMPONENTS

Resin/Material	% Initiator	Minutes Time to T_{max}	T_{max},°F	Barcol	Comments
1. 15-1562 polyester- (Cargill)	0.4	3.1	244	50	dry
2. 15-1554 vinyl ester(Cargill)	0.4	1.9	193	-	tacky
3. 15-1554 plus 20% styrene(additional)	0.4	2.0	272	-	wet
4. Nupol 046-4440 (Freeman)	0.4	2.3	179	38	tacky
5. Nupol 046-4005 (Freeman)	0.4	3.2	139	-	wet
6. VE 8730-34(Interplastic) special novolac	0.4	2.8	173	40	wet
7. VE 8750 (Interplastic) BPA epoxy acrylate (320°F heat deflection)	0.4	3.0	255	42	dry
Evaluation of the Effect of Selected Monomers					
8. 31351 (Reichhold) (same as Koppers 9200NP)	0.4	7.0	196	38	dry
--plus 10% 1,4-butanediol dimethacrylate		6.9	285	30	tacky
- plus 10% 1,4-butanediol diacrylate		6.6	225	37	tacky
-- 10% tripropylene glycol diacrylate		7.9	215	-	wet
-- 10% trimethylolpropane ethoxy triacrylate		6.0	236	32	tacky
-- 10% trimethylolpropane triacrylate		6.1	210	30	tacky
-- 10% divinyl benzene		8.3	225	26	dry
-- 10% hydroxypropyl methacrylate		6.6	233	24	dry
9. Ebecryl 629-novolac		4.0	217	50	tacky
-- 10% 1,4-butanediol diacrylate		2.2	172	-	light tack
-- 10% hydroxypropyl acrylate		2.9	218	-	tacky

Vinyl BPA and Novolac Ester Resins. All of the vinyl novolac ester resins which we could obtain were evaluated as they were received. Many low color high quality vinyl BPA ester resins along with other new resins were also evaluated as part our continued search and evaluation in case there was some resin type or blend that we may have overlooked.

The two compounded vinyl novolac resins from Radcure, 629 which performed well and was described previously and 639 gave an insight as to why the novolac resins gave faster cure rates. 639 has a higher acrylate functionality per molecule of 3.6 which explains the more rapid cure (Time to T_{max} of 2-3 minutes) compared to 629 which has a functionality of 2.2 with a Time to T_{max} of 4 minutes. This effect of faster cures with higher functionality is general and accounts for the enhanced effect of polyfunctional monomers which will also be discussed.

Although Radcure 639 (vinyl novolac) was blended with various monomers including 10-20% styrene, hydroxypropyl methacrylate, hydroxypropyl acrylate, or trimethylol propane triacrylate, there was no improvement in cure or properties. It was already multifunctional, and perhaps had achieved its maximum cure rate. However, VE 875 (Interplastic vinyl BPA ester containing styrene) when blended with 30% pentaerythritol tetraacrylate decreased Time to T_{max} from 3.0 to 2.2 minutes which was significant and due to the multfunctionality. Therefore, both multifunctionality in the backbone molecule and in the monomer diluent can speed up the rate of cure. This was another guideline to utilize in the development of the most rapidly photocuring resin system.

A sample of Derakane 411-45(Dow) was specially requested which had low inhibitor and was light in color. This basic vinyl BPA resin cured more rapidly than previous lots of 411-45 (Time to T_{max} decreased to 4.1 minutes and with a dry surface). Blending this styrene containing resin with hydroxypropyl or hydroxyethyl acrylate did not change the cure rate, but the Barcol was lowered due the greatly diminished backbone resin concentration. The addition of 20% pentaerythritol tetraacrylate significantly reduced the Time to T_{max} to 2.8 minutes and increased the Barcol from 38 to 44 while giving a tack free surface. This meant that the multifunctional acrylates (tetraacrylates) could be used in conjunction with clean light colored base resins (both vinyl BPA and novolac types) to achieve rapid cure systems. The novolacs were selected for their inherently higher heat distortion temperature, faster cure rate in general, and other physical properties. However, satisfactory performance could be obtained with the vinyl BPA based resins.

Several other commercial vinyl BPA resins were evaluated and as expected were relatively slow, but all cured to a dry surface in air. These evaluations are listed in Table 6.

The tensile strength was determined on Derakane 470-36 which was photocured under nitrogen. This was the first vinyl novolac that we had found to cure rapidly, but incompletely in air. The tensile strength was 11,500 psi which corresponded to the published value for the peroxide cured resin. This again confirmed that the tensile strength for a given resin is not affected negatively by this photocure system.

TABLE 6
PHOTOCURE RATES FOR VARIOUS VINYL ESTER RESIN COMPONENTS

Resin/Material	% Initiator	Minutes Time to T_{max}	T_{max}, °F	Barcol	Comments
1. Ebecryl 8800	0.4	3.3	153		sl.tacky
(Acrylated polyurethane--potential use for adhesive layer for patch when repairing metal surfaces and urethane painted surfaces if needed.)					
2. Ebecryl 8800	0.6	2.6	162	-	tack
3. Derakane 411-45 (new lot)	0.4	4.4	239	40	dry
4. Derakane 411-45 (new lot)	0.6	4.1	218	38	dry
5. Ebecryl 639	0.4	2.0	177	-	tacky
(vinyl novolac with high functionality and light color.)					
6. Ebecryl 639	0.6	3.3	158	-	tacky
7. Aropol L-2530T-20 (Ashland)	0.4	8.2	182	40	dry
8. Ashland 99P	0.4	9.7	177	32	dry(colored)
9. Koppers 6246 (polyester resin)	0.4	5.9	242	44	dry
Evaluation of the Effect of Selected Monomers Added to Resins.					
10. 8800 + 15% styrene	0.4	3.3	191	-	tacky
--plus 35% TMPTA	0.4	2.1	196	-	tacky
--plus 35% hydroxy propyl methacrylate	0.4	1.4	194	-	tacky
11. Ebecryl 639 -10% TMPTA	0.4	3.0	180	-	sl. tack
-plus 10% hydroxypropyl methacrylate(HPMA).	0.4	2.2	220	-	sl. tack
--plus 20% HPMA	0.4	3.4	195	-	sl. tack
--plus 20% styrene	0.4	2.9	239	-	tacky
--plus 30% styrene	0.4	2.7	250	-	tacky
--plus 40% styrene	0.4	4.2	301	-	tacky

TABLE 4 (CON'T)

12. VE 8750(Interplastic) 10% hydroxypropyl acrylate	0.4	3.6	270	40	tacky
(standard VE 8750 was	0.4	3.0	247	40	dry)
13. VE 8750(Interplastic) plus 10% hydroxypropyl methacrylate	0.4	4.1	268	42	tacky
14. VE 8750 plus 30% pentaerythritol tetraacrylate	0.4	2.2	273	40	tacky
15. 411-45 plus 20% hydroxypropyl acrylate	0.4	4.5	297	32	dry
16. 411-45 plus 20% hydroxyethyl acrylate	0.4	4.2	285	32	dry
17. 411-45 plus 20% pentaerythritol tetraacrylate	0.4	2.8	256	44	dry
18. 411-45 plus 30% pentaerythritol tetraacrylate	0.4	2.6	308	42	dry

Several additional vinyl BPA resins from Interplastic and Silmar were evaluated. (See Table 7.) Of these resins, the VE8770 (Interplastic) was the fastest and cured tack-free in the air with a Barcol of 46. Both the Silmar S-40 and the Interplastic VE8151 had Barcols over 40 and cured in less than five minutes. A new novolac from Radcure(RSX88210) diluted with 40% styrene was found to cure in 2.9 minutes.

The acrylated vinyl novolac with high functionality was selected as the prime candidate resin base stock for the resin for the field repair patch. Special custom one-gallon samples of this resin were ordered from Cargill, Interplastic, and Monomer-Polymers, Inc. with the stipulation that the resins be as light colored as possible, no additives, and have low inhibitor levels. These were to be based on Shell Epon DPS-155 epoxy novolac (functionality = 3.6). After receiving these resins, we planned to formulate with different monomers to determine the best monomer blend for the resin.

Monomer Evaluation: A series of resins were run with vinyl toluene to evaluate this relatively common lower volatility monomer and the results are listed in Table 8. The results for the same resin without vinyl toluene are given in parentheses below these results. Depending on the resin, the vinyl toluene appeared to cause no change or improvement in the surface cure. It can speed up the cure when no other monomer is present such as in the case of Radcure 616.

Vinyl toluene was evaluated as a higher boiling replacement for styrene in these resin systems particularly when trying to improve the Barcol, and possibly rate of cure.

A side by side evaluation of the effect of the addition of multifunctional acrylates was performed to be sure of the relative effects of dipentaerythritol pentacrylate (DIPETA)(5 functional groups), pentaerythritol tetracrylate (PETA)(4 functional groups), trimethylolpropane triacrylate (TMPTA)(3 functional groups), and 1,4-butanediol diacrylate (2 functional groups). The multifunctional acrylates particularly PETA, DIPETA, and TMPTA all decreased the time to reach T_{max} by about 40% and increased the Barcol.

TABLE 7
PHOTOCURE RATES FOR VARIOUS VINYL ESTER RESIN COMPONENTS

Resin/Material	% Initiator	Minutes Time to T_{max}	T_{max}, °F	Barcol	Comments
1. VE8770 (Interplastic)	0.4	3.2	234	46	dry
2. VE8440 (Interplastic)	0.4 0.6	6.1 5.8	231 262	32 32	dry dry
3. VE8520 (Interplastic)	0.4	7.1	207	28	tacky sur.
4. VE8300B-35 (Interplastic)	0.4	4.8	220	34	dry
5. VE8151 (Interplastic)	0.4	4.3	179	42	dry
6. VE8710 (Interplastic)	0.4	6.7	214	40	dry
7. S-40(Silmar)	0.4	4.9	236	44	dry
8. RSX88210 (Radcure) Novolac(added 40% styrene as monomer)	0.4	2.9	191		tacky surface
9. Dipentaerythritol Pentacrylate	0.4	1.6	271	65	dry
10. 6661-0(RohmTech) polyamide type diacrylate; possibly useful for additional adhesion if necessary.	0.4	1.7	163	40	tacky sur.

TABLE 8
RESIN AND MONOMER BLENDS

Resin	Monomer(%)	Initiator%	Time to T_{max}	T_{max}, °C	Barcol	Comments
1. 629	vinyltoluene(20)	0.4	3.1	201		tacky sur.
(Radcure)			(3.2)	(190)		tacky sur.
2. 616	"	0.4	2.9	165		"
(Radcure)			(5.3)	(163)		"
3. 470-36	"	0.4	4.7	278	44	dry!
(Dow)			(4.4)	(188)		wet
4. VE8730-34	"	0.4	4.0	255	48	dry
(Interplastic)			(4.0)	(228)		tacky sur.
5. 31351	"	0.4	7.8	232		sl.tacky sur.
(Koppers)			(7.8)	(247)	40	dry
6. 629	pentaerythritol	0.4	2.9	219	48	tacky sur.
	tetracrylate(20)	(PETA)	(3.2)	(190)		"
7. VE8730-34	"	0.4	2.8	232		tacky surface
			(4.0)	(228)		"
8. 470-36	"	0.4	3.2	179		"
			(4.4)	(188)	43	"
9. 639	"	0.4	2.4	178		tacky surface
			(3.4)	(178)	42	"
10. 411-45	"	0.4	2.8	323		brittle and dry
(Dow)			(4.7)	(253)	40	tacky sur.
11. "	dipentaerythritol	0.4	2.6	293	42	dry
	pentacrylate(20)		(4.7)	(253)	40	tacky sur.
12. "	" (10)	0.4	3.6	321	44	dry
			(4.7)	(253)	40	tacky
13. 15-1562	(PETA)(20)	0.4	2.8	310	55	dry
(Interplastic)			(3.1)	(244)	50	dry
14. "	trimethylol	0.4	2.4	283	54	dry
	propane triacrylate (20)		(3.1)	(244)	50	dry
15. "	1,4-butanediol	0.4	2.8	310		v.sl.tacky
	diacrylate(20)		(3.1)	(244)		dry

A comparison was done between the effects of adding DIPETA(five functional acrylate) and the related pentaerythritol triacrylate(three functional)(PETRIA) in order to further determine if the degree of functionality on a monomer above two or three is important as far as cure rate or other characteristics are concerned. In Table 9 are listed the results of this comparison with several different vinyl resins. There was no question that these two polyfunctional acrylates significantly improved the rate of cure, except with VE8770 which is already a fast vinyl resin. It appears that there is a slight improvement in cure rate for the five functional monomer over the three functional monomer. This effect is very dependent on the resin.

TABLE 9
EFFECT OF PENTA- AND TRIFUNCTIONAL ACRYLATES ON RESIN CURES
(DIPETA) (PETRIA)

Resin	Monomer(%)	Initiator%	Time to T_{max}	T_{max},°C	Barcol	Comments
1. 411-45 Dow	DIPETA(20)	0.4	2.6 (4.7)	293 (253)	42 (40)	bot. wet
Previously	PETRIA (20) gave		2.8	323		very brittle
2. 411-45	" (10)	0.4	3.6	255	44	" "
3. 470-36	" (20)	0.4	3.1 (4.4)	171 (188)	(43)	tacky surf.
4. 470-36	PETRIA (20)	0.4	3.1	217		" "
5. 31351 (Koppers)	" (20)	0.4	4.9 (7.8)	278 (247)	(40)	" "
6. 31351	DIPETA(20)	0.4	3.8	199	39	
7. VE8770 Interplastic	" (20)	0.4	3.5 (3.2)	226 (234)	(46)	tacky surf.
8. VE8770	PETRIA(20)	0.4	3.0	278		" "

Cargill resin 15-1562 is a relatively fast unsaturated polyester resin formed from propylene glycol and maleic anhydride. It was found to decrease its reactivity over time. This was one of few commercial resins which we had received where many of the usual variables were not present, and yet its rate inexplicably changed. We thought that if some simple additive would restore the original activity of this resin it would provide the clue as to what causes the usual batch to batch variation in the commercial resins which we had evaluated. This resin was evaluated with a number of different additives with some interesting results as reported in Table 10. We found that organic bases significantly slowed down the photocure. On the other hand, an organic acid(maleic anhydride) appeared to speed up the resin cure. The acid number of this resin did decrease with time. We demonstrated that there is an optimum amount of monomer or monomer mix that should be added to a given resin. In this case 40% appears to be a good level for Barcol and rate. The acid number might be a truly important variable for rate and the nature of the cure. It might be easier to always add a certain quantity of organic acid to make sure that this is no longer a variable with which to be concerned.

TABLE 10
EFFECT OF ADDITIVES ON CARGILL 1562 RESIN CURES

Additive(wt%)	Time to T_{max}	T_{max},°C	Barcol	Comments
Reference no additives (35% styrene)	3.8	213	50	
1. vinyl toluene(10)	3.0	172	43	not tacky
2. maleic anhydride(0.5)	3.5	183	43	" "
3. " " (1.0)	3.1	173	45	"
4. tributyl phosphine(1.0)	3.8	212		tacky surf.
5. N,N-diethylaniline(0.5)	7.0	130	42	
6. hydrazine hydrate (0.5)	5.1	136	25	
Base stock resin for 1562--styrene free at start prior to adding additives.				
8. styrene (30)	4.6	228	47	
9. " (40)	3.4	208	49	
10. vinyl toluene(30)	4.6	198	47	
11. " " (40)	3.0	190	49	

An evaluation of the variations in cure rate for Cargill 15-1562 showed that the addition of some types of acids, toluene sulfonic, maleic, and even acetic, would speed up the cure rate. About 1% acetic acid did improve the cure rate. Water caused some slowing although not in the presence of the acids. (See Table 11.) It was shown that the resin should have a high acid number or even add 0.5% to 1.0% acetic acid or acrylic acid to the final resin mixtures.

TABLE 11
EFFECT OF ADDITIVES ON CARGILL 1562 RESIN CURES
(0.4% Initiator)

Additive(wt%)	Time to T_{max}	T_{max}, °C	Barcol	Comments
Reference 1562 no additives (35% styrene)	3.8	213	50	
1. styrene(65)	3.3	240	46	brittle
2. 1,4-butanediol diacrylate(30) (no styrene)	4.7	185	36-38	brittle
3. styrene(30);toluenesulfonic acid(2)	3.8	172	38-40	wet bot.
4. styrene(30);acetic acid(0.5)	3.6	208	44-46	brittle
5. styrene(30);PETA(20); acetic acid(1)	2.6	198	50-52	dry cure
6. styrene(30);PETA(20); acetic acid(0.50)	3.2	228	46-48	dry cure
7. styrene(30);PETA(20); toluenesulfonic acid(0.3)	2.6	196	48	tacky

Further testing of the effect of acid and water and several other additives was done on a vinyl ester(Derakane 411-45) and an unpromoted ortho ester (Silmar S-4A). These results are listed in Table 12 and confirmed the positive effect of small amounts of acetic or acrylic acid on the cure rate. Several polyfunctional acrylate additives were also evaluated and found to speed up the cure rate as expected.

When we tested the cure rate under nitrogen purge, the rate significantly increased as can be seen in the examples in Table 13.

TABLE 12
EFFECTS OF ADDITIVES ON DERAKANE 411-45 AND SILMAR S-4A

Additive(wt%)	Time to T_{max}	T_{max}, °C	Barcol	Comments
Reference resin S-4A styrene(40);cat.(0.4)	4.5	203	40-42	dry cure
1. hydroxyethyl acrylate(10)	3.9	215	44-46	"
2. water(0.5)	4.8	143	48-50	"
3. acetic acid(1)	4.6	167	46	"
4. acetic acid(1);water(0.5)	4.0	209	44-46	"
5. PETA(10)	3.2	227	44-46	"
	2.8	232	50	"
6. 1,4-butanediol diacrylate(10)	4.0	245	48-50	"
7. TMPTA(10)	3.3	237	48-50	"

TABLE 12 (CON'T)

8. acrylic acid(1)	4.0	235	44	"
9. Hydroxypropyl acrylate(20)	3.7	211	34-36	"
10. Hydroxypropyl methacrylate (20)	4.3	210	34-36	"
Reference 411-45	4.8	197	36-38	"
11. acetic acid(1)	4.0	272	36-38	"
12. water(0.5)	4.5	267	32-34	"
13. maleic anhydride(1)	5.7	234	36-38	"
14. maleic anhydride(1); water(0.5)	5.1	235	32-34	"

TABLE 13
EFFECTS OF ADDITIVES ON DERAKANE 411-45 AND SILMAR S-4A

Additive(wt%)	Time to T_{max}	T_{max},°C	Barcol	Comments
Reference resin S-4A styrene(40);cat.(0.4)	4.5	203	40-42	dry cure
1. hydroxyethyl acrylate(20)	4.4	231	42	"
2. " " (under nitrogen)	2.9	223	41	"
3. " " (plus 1% acrylic acid)	3.9	239	40	"
4. " " (plus 1% acrylic acid and under nitrogen)	2.5	151	40	"
5. Hydroxypropyl methacrylate(20) (plus 1% acrylic acid)	3.9	214	45	"
6. " " (plus 1% acrylic and under nitrogen)	2.6	210	45	"
Reference 411-45(new batch)	5.3	206	40	"
7. Hydroxyethyl acrylate(20)	5.3	285	36	"
8. 1,4-butanediol diacrylate(20)	5.3	330	41	"
9. Trimethylolpropane triacrylate (20)	4.1	327	43	"
10. Pentaerythritol tetracrylate (20)	3.3	268	45	"

Other new resins and monomers and frequent rechecks on some monomers were run on an ongoing basis. These results are listed in Table 14. The alkoxylated triacrylate (Sartomer 9008) was unusually fast, but it would not have high tensile or high temperature properties. The special OCF resin was very fast but it is a maleic acid /propylene glycol polyester resin(low color). It would not have good high temperature properties although it would be good as an adhesion promoter when blended in another resin.

TABLE 14
EVALUATION OF OTHER NEW RESIN AND MULTIFUNCTIONAL MONOMERS
(0.4% Initiator)

Resin	Time to T_{max}	T_{max},°F	Barcol	Comments
1. Alkoxylated triacrylate (Sartomer 9008)	1.4	267		very brittle
2. 1,4-butanediol diacrylate (Sartomer 213, recheck)	1.4 (aver. of 3 runs)	>400		"
3.1,4-butanediol dimethacrylate (Sartomer 214, recheck)	2.3	307		"
4.Polyethylene glycol 600 dimethacrylate(Sartomer 252)	1.8	182		soft
5. Polyethylene glycol 400 Diacrylate(Sartomer 344)	1.7	232		soft
5.Pentaerythritol tetraacrylate (Sartomer 295, recheck)	2.0	300		
6. Ethoxylated Bisphenol A Diacrylate (Sartomer 349, recheck)	2.6	233		wet bottom
7.Trimethylolpropane triacrylate (Sartomer 351, recheck)	1.9	418		brittle
8.Trimethylolpropane trimethacrylate(Sartomer 350, recheck)	3.6 3.6	217 217		
9. Dipentaerythritol hydroxypentacrylate(Sartomer 399, recheck)	2.0	281		brittle
10. Triacrylate ester (Sartomer 9012)	1.7	234		brittle
11. CX1751T (OCF)/35 % styrene maleic anhydride/propylene glycol polyester	3.1	337	40	
12. " "/35% vinyl toluene	2.7	169	40	

Resin Development and Optimization. The three specially requested custom resins were received from Monomer-Polymer (9459), Interplastic (VEX168-404), and Cargill (158-1721). Only Cargill followed our specific instructions for the synthesis which were:

a. Use Shell Epon DPS-155 Novolac Epoxy resin;
b. Use no metal cation in the synthesis as a catalyst for acrylation;
c. Use only a minimum of heating(180-200°F) and do not finish off by over heating, prolonged heating, or adding strong acid.

The Cargill resin was the lightest in color and had a high acid number (desirable).

The results of the evaluation of these resins are shown in Table 15. It was gratifying to see that all three resins cured under three minutes as predicted, and that the Cargill resin was the fastest of any vinyl resin that we had evaluated with only styrene as the monomer. The cure rate for the Cargill resin #1721 was T_{max} of 2.2 minutes without optimizing.

The goal of identifying and producing an optimized vinyl ester resin which cures very rapidly was accomplished at this point. The corresponding blending monomer(s) and the amounts needed to be determined. However, the initial performance of #1721 with 30% styrene was already outstanding with respect to cure rate.

Cargill was asked to scale up this resin to a one gallon size to see how reproducible this resin was and to obtain enough for significant evaluation and complete the formulation work. (The first batch was only about a pint of material.) We eliminated the resin from Interplastic because it appeared to contain some inhibiting or light absorbing catalyst from the acrylation step which prevented the light from penetrating to the bottom of the 0.25-in. depth of resin which we use as a standard. They did not use the DPS-155 epoxy Novolac or acrylation catalyst which we requested. The Monomer-Polymer resin could be used as a back up candidate, but it was a little slower than the Cargill #1721, and they did not manufacture commercial quantities.

TABLE 15
EVALUATION OF NEW VINYL NOVOLAC RESINS

Resin	Initiator%	Time to T_{max}	T_{max},°C	Barcol	Comments
1. 9459(MonomerPolymer) (acrylated novolac glycidyl ether -25% styrene)	0.4	2.8	258	37-39	cures dry
2. " " (acrylated novolac glycidyl ether-30% hydroxyethyl acrylate)	0.4	2.9	267	38-40	"

TABLE 15 (CON'T)

3. 158-1721(Experimental) (acrylated special novolac made for Sunrez by Cargill plus 30% styrene)	0.4	2.2	260	42-44	cures dry
4. VEX168-404 (Interplastic) (epoxy novolac vinyl ester resin with 35% styrene)	0.6	2.8	144	44-46	wet bottom
5. VEX168-405 (Interplastic) (epoxy novolac vinyl ester resin plus 35% styrene)	0.6	7.6	151	46-48	" "

Two additional small batches of 1721 were received from Cargill (#64 and #66). These two runs were evaluated to determine the kind of variation from batch to batch and what other specifications to place on the resin prior to making larger batches. Table 16 lists the results of checking these lots under several conditions. There is some variation in the results in Table 16, but generally certain conclusions can be drawn. Batch #64 was higher molecular weight and slightly higher in color. It also cured on the average slightly slower and was softer on curing than the original batch #65. Batch #66 was lower in molecular weight and appears to be slightly slower than batch #65. Batch #66 would have been acceptable except that the molecular weight would have been a concern. It appears that 30 to 40% styrene is an acceptable amount of styrene for this resin. The photoinitiator level should be about 0.4% as expected. About 1% acrylic appears to help in certain cases, higher levels do not help. The Barcols ranged from 42 to 49 depending on conditions.

In discussions with Cargill, it appeared that the critical parameter was the color and the molecular weight. Both of these parameters are a function of heating too long or not long enough at a given temperature. We agreed on a specific length of time and to follow the reaction by means of the amount of free acid remaining.

An evaluation is listed in Table 17 concerning of the effect of 35% of various monomers on batch #65. Only 1,4-butanediol diacrylate permitted #65 to cure as fast as with styrene (2.2-2.6 minutes). Vinyl toluene (mixed meta and para from Dow) and para-vinyl toluene gave about the same result which was slightly slower than styrene. Trimethylolpropane triacrylate was much slower than expected and this might be attributable to the increased viscosity of the pure resin since there is no styrene present to cut the viscosity. Vinyl toluene, 1,4-butanediol diacrylate along with styrene appeared to be acceptable monomers for blending with Cargill 1721.

TABLE 16
EVALUATION OF SAMPLE LOTS OF NEW CARGILL VINYL NOVOLAC RESIN WITH STYRENE

Additive(wt%)	% Initiator	Time to T_{max}	T_{max}, °F	Barcol	Comments
Reference resin 1721					
Initial batch(65) best so far (m.w.=1205);					
Second batch(64) slightly more color; higher m. w. 1799					
Third batch(66), (m.w.=850) light in color, slightly under reacted					
65					
1. 30% styrene	0.4	2.2	180	46	
2. "	0.2	2.5	260	43	
3. "	0.6	2.7	222		
4. "	0.3	2.2	219	43	
5. " " plus 1% DER 330 epoxide	0.4	2.5	245	45	
6. 35% styrene	0.4	2.5	208	44	
7. " "	0.2	2.9	230	44	
8. " "	0.6	2.8	189	42	
9. " " (1% acrylic acid)	0.4	2.5	204		
10. " " plus 2% acrylic acid	0.4	2.6	193	45	
11. 40 % "	0.4	2.1	265	46	
64					
12. 30% styrene	0.4	2.8	201	42	
13. 35 % "	0.6	3.3	186	43	
14. " "	0.4	2.4	176	45	
66					
15. 30% styrene	0.4	3.4	226	45	
16. 35% "	0.4	2.8	239	45	
17. 35% "	0.6	2.9	227	44	
18. 35% styrene plus 1% acrylic acid	0.4	2.7	255		
19. " " plus 2% acrylic acid	0.4	3.5	282	44	
20. 40% "	0.4	3.4	266	4	

TABLE 17
EVALUATION OF CARGILL 158-1721 -65 WITH VARIOUS MONOMERS
(35 % monomer)

MONOMER, % (0.4% initiator)	Time to T_{max}	T_{max}°F	Barcol	Comments
1. 1,4-butanediol diacrylate	2.3	200		
2. " " plus 1% acrylic acid	2.5	182		
3. p-vinyl toluene	2.9	234	42	
4. " " plus 1% acrylic acid	2.7	237	40	
5. vinyl toluene(Dow)	3.2	215	49	
6. trimethylolpropane triacrylate	4.2	201	44	

Further examination of the initial batches of the Cargill custom batches of the special vinyl novolac resin, showed that the optimum rate was with a styrene concentration of 35%. (The results are listed in Table 18.) The reason for this optimum range may be that too little monomer (styrene in this case) causes the viscosity to be too high and starves the initiating sites on the backbone molecule for the chain propagating styrene. Too much styrene slows the reaction due to increased air sensitivity of the growing polystyrene chains, and the styrene acts as a diluent and less as a reactant. The optimum balance in this case appeared to be the 35% level found. The addition of 1% acrylic resin slowed the rate in the case of the optimum batch #65 (the first one) which already had a slight excess of acid. Evidently the positive effect of the acrylic acid was simply to have a slight excess of organic acid, and then it was of no further benefit. (See Table 18.)

The scaled up next batch of special resin (#72) was only about 10 pounds, but it was examined it to see if it duplicated the previous runs with respect to photocure rate. During manufacture, it was heated the minimum time in the reactor at 180°F. The material was as light colored as any we had received. In the initial cure rate test which was run several times with 35% styrene, the Time to T_{max} was about 3.4 minutes. Although this was acceptable, it was a full minute slower than the previous batches. Discussions with the Cargill laboratory produced only one plausible explanation. In these acrylation reactions or any of the esterification reactions forming vinyl esters, a fixed amount of inhibitor such as hydroquinone is added in order to prevent condensation of the resin product while the reaction is taking place. The amount of inhibitor is determined empirically by previous experience so as to add just the right amount to prevent polymerization in the reactor, yet not so much as to prevent subsequent polymerization of the resin.

The photoinitiated reaction of the resin was found to be sensitive to inhibitors and gradually slowed down when the concentrations rose above a few hundredths of a percent. In the case of the acrylation reaction of the epoxides, the inhibitor slowly reacted away also with the epoxide present, particularly in the presence of the tetramethylammonium hydroxide catalyst used. If the reaction is cut off earlier or if there is a shorter reaction time than normally expected, a higher level of inhibitor than normally expected will be remaining at the end of the reaction. This higher level will slow down the photoinitiated reaction rate of in the product resin. (This effect was also seen in the stability studies of these resins.) In order to demonstrate this and possibly finding a way to speed up a resin system which has too much inhibitor for our purposes, we added 1-2% DER 330 to #72 batch of the special vinyl novolac resin. The DER is a BPA diepoxide and will react with hydroquinone or other such inhibitor when warmed especially in the presence of tetramethylammonium hydroxide catalyst. Room temperature addition produced no effect, but heating at 150°F for 10-15 minutes did cause a significant reduction in Time to T_{max} to the rate normally experienced by batch #65 and batch #66. The Time to T_{max} for all of these acrylated Novolac resins appears to converge in the 2.2 to 2.8 minute range. In fact, no base stock resin system which was tested cured faster, although several acrylate monomers did go faster. (It is important to remember that our test light was set up to give about the same effective UV_a amount as sunlight per unit area. Higher wattage lamps dramatically shorten the cure time.)

TABLE 18
EVALUATION OF SAMPLE LOTS OF NEW CARGILL VINYL NOVOLAC RESIN WITH STYRENE

Additive(wt%)	% Initiator	Time to T_{max}	T_{max},°F	Barcol	Comments
Reference resin 1721					
Initial batch(65) best so far (m.w.=1205);					
second batch(64) slightly more color; higher m. w. 1799					
third batch(66), (m.w.=850) light in color, slightly under reacted					
fourth batch(72) ran minimum time possible					
65					
1. 30% styrene plus 1% acrylic acid	0.4	3.2	262	46-48	
2. 35% " plus 1% acrylic acid	0.4	2.6	245	40-42	
3. 40% " plus 1% acrylic acid	0.4	3.0	271	42	
4. 30% " rerun as a check	0.4	2.6	182	42	

TABLE 18 (CON'T)

66				
5. 35% "	0.6	2.6	230	43
6. 35% "	0.4	2.7	230	42
7. 40% "	0.4	2.8	265	42
8. 30% "	0.4	2.9	196	44
64				
9. 30% "	0.4	3.0	254	42
10. 35% "	0.4	3.0	286	40-42
11. 40% "	0.4	4.1	283	40
72-new lot				
12. 30% "	0.4	3.5	272	40
13. 35% " (average of two runs)	0.4	3.4	250	42
14. 35% " plus 2% DER 330	0.4	3.1	271	42-44
15. same as #11 with warming at 150°F for 10 min.	0.4	2.5	215	40
16. 35% " plus 0.1% tetramethylammonium hydroxide	0.4	3.7	222	44

In summary, the critical factors for rapid cure are: resin color, the basic resin structure, the amount of inhibitor, absence of metal catalysts and accelerators, percent monomer, monomer structure, and initiator level. These are all factors which have been investigated with different resins and under a variety of conditions.

The fastest photocure resin system available from a structural and patching point of view has been achieved. This resin system could be speeded up to curing in a few seconds if we used very powerful UV lamps such as might be used on a production line. However, when using the weaker portable (100 watt) light which is and operated off a vehicle battery or by sunlight, we have still achieved a very rapid cure under field conditions. This special acrylated vinyl novolac plus the several backup vinyl BPA and polyester resins can satisfy most reasonable requirements for a field repair system.

The largest size batch(ten pounds) of the special vinyl ester novolac resin (#72 from Cargill) was retested to be sure of the experimental conditions and to determine that it could be modified to improve its rate of cure. This batch apparently contained more inhibitor than previous lots and that the use of the diepoxide(DER 330) was a way to compensate for this. Too much DER 330 as seen in Table 19 had a negative effect and therefore the addition should be no more than 1%. The four lots of this special vinyl novolac ester resin were combined in order to produce enough of this resin for a group of twelve prototype patch kits. In this step the resin must be heated and then diluted with styrene to the desired level. The Time to T_{max} for this combination after additional heating fell to about two minutes which is the fastest that we have had achieved for any of these structural type vinyl ester resins with styrene as the monomer. This again demonstrated that some of the previous batches had not been heated enough which probably left too high a level of inhibitor in those batches at the end of the preparation.

TABLE 19
EVALUATION OF SAMPLE LOTS OF NEW VINYL NOVOLAC RESIN (CARGILL)
(includes repeats of some previous runs)

Resin(Additive%)	%Initiator	Time to T_{max}	T_{max},°F	Barcol	Comments
65					
(35% styrene)	0.4	3.0	186	44	
(35% styrene, 2% Tetramethylammonium hydroxide)	0.4	2.7	193	43	
(25% styrene, 10% hydroxypropyl acrylate)	0.4	3.4	272	44	
(25% styrene, 10% 1,4-butanediol diacrylate)	0.4	2.6	221	45	
66					
(35% styrene)	0.4	3.0	260	42	
(25% styrene, 10% 1,4-butanediol diacrylate)	0.4	3.0	279	42	
(25% styrene, 10% hydroxypropyl acrylate)	0.4	3.0	237	42	
(25% styrene, 10% trimethylolpropane triacrylate)	0.4	3.0	227	47	
(35% vinyl toluene - Dow)	0.4	3.0	237	42	
(25% vinyl toluene, 10% 1,4-butanediol diacrylate)	0.4	2.5	253	43	

TABLE 19 (CON'T)

(25% vinyl toluene, 10% hydroxypropyl acrylate)	0.4	2.6	221	42
<u>72</u>				
(35% styrene)	0.4	3.3	243	45
(34% styrene, 1% DER 330-diepoxide)	0.4	2.9	238	45
(33% styrene, 2% DER 330-diepoxide)	0.4	3.3	287	45
<u>Combined Batch</u>				
(20% styrene)	0.4	2.2	216	47
(35% styrene)	0.4	1.8	239	42

<u>Other Backup Resins.</u> One of the lightest colored polyester resins examined was a polypropylene maleate base stock (CX1751T from OCF). It was relatively fast for an unsaturated polyester although it did form relatively brittle cured resins. It could be modified if necessary with the addition of acrylated polyurethanes or related resins or monomers. (See Table 20.) It was also a good candidate for the adhesive putty.

TABLE 20

EVALUATION OF OTHER NEW RESINS AND MULTIFUNCTIONAL MONOMERS

(0.4% Initiator)

Resin	Time to T_{max}	T_{max}, °F	Barcol	Comments
All runs with CX1751T (OCF propylene maleate clear resin) plus 0.4% photoinitiator				
1. Styrene 45%	3.2	337	45	brittle
2. " 40%	3.1	303	44	"
3. " 35% (average two runs)	3.4	271	46-48	"
4. " 30%	2.9	228	44-46	"
5. " 25%	3.5	200	44-46	"
6. " 34%; 1,4 butanediol diacrylate 5%	3.2	300	48-50	"
7. " 25% hydroxyethyl acrylate 20% 1,4-butanediol diacrylate 10%	3.0	247	40	"
8. " 25% hydroxypropyl methacrylate 20% 1,4-butanediol diacrylate 10%	2.7	284	44	"

A check was made of the effect of adding DER 330(diepoxide) on two commercial resins which were not vinyl ester resins and with which we had experience. (See Table 21.) There was no effect and we assumed that the inhibitor levels were as low as we had requested for these commercial resins.

TABLE 21
EVALUATION OF OTHER RESINS WITH DER 330 (DIEPOXIDE)
(0.4% photoinitiator)

Resin (%DER 330)	Time to T_{max}	T_{max}, °F	Barcol	Comments
VE 8750 (Interplastic)	4.5	240	38	
VE 8750 (1%)	4.5	175	45	
VEX168-429 (Interplastic)	4.4	239	45	
VEX168-429 (1%)	4.5	248	44	

Several additional commercial vinyl ester resins (BPA-based) were evaluated as backup candidates and alternates in case of any problems with the preferred resin. Both 15-1574 and 15-1575 from Cargill and VEX 168-429 (Interplastic) were evaluated and the results are given in Table 22. 15-1574 responded very well and gave good cures similar to Derakane 411-45 which is a primary backup resin. However, 15-1574 reached Time to T_{max} in 3 or less minutes whereas 411-45 requires 4.5 to 5 minutes to accomplish this. Therefore, this resin is considered a preferred backup vinyl ester resin. In addition, 15-1574 is available as the base stock resin which permits choice of the monomer and the amount of monomer to any desired level. The base stock resin for Derakane 411 was not available.

TABLE 22

EVALUATION OF COMMERCIAL VINYL ESTER RESINS AS BACKUP TO THE NEW VINYL NOVOLAC RESIN (CARGILL)
(0.4% photoinitiator)

Resin(Monomer%)	Time to T_{max}	T_{max}, °F	Barcol	Comments
15-1574(20% styrene) (Cargill)	3.2	197	47	
15-1574(20% vinyl toluene)	2.7	204	47	
" (30% styrene)	2.7	260	46	
" (35% styrene)	2.7	178	47	
" (40% styrene)	3.1	223	44	

TABLE 22 (CON'T)

15-1575(25% styrene)	2.6	235	45	tacky surface
" " (used 0.6% photoinitiator)	3.0	212	45	" "
15-1575(35% styrene)	3.4	304	45	" "
" (35% vinyl toluene)	3.1	268	46	" "
" (40% styrene)	4.2	339	45	" "
" (40% vinyl toluene)	3.0	300	46	" "
" (45% styrene)	4.9	251	46	" "
VEX168-429(35% styrene)	4.3	225	45	" "

Final Development of Monomer Component of Selected Resin System. An evaluation of the effect of styrene versus vinyl toluene (Dow-which is mainly meta isomer) with respect to the cure rate on batch #66 (Cargill) was made. (See Table 22.) Although there was no difference between styrene and vinyl toluene at the 35% level, there was an acceleration in the case of vinyl toluene at 25% plus 10% added acrylate monomer as compared with styrene. Vinyl toluene was a satisfactory replacement for styrene in the vinyl ester novolac resins for the "patch" system. This permits a higher boiling point monomer if needed. The addition of acrylate and polyfunctional acrylate monomers did not always increase the cure rate for the vinyl ester novolac resins. It appeared that the cure rate for all of these fast resins could not be significantly improved. Therefore, the rate for these faster resins with 35% styrene will usually be in the 2-3 minute range. 1,4-butanediol diacrylate did improve the rate somewhat in several cases and made a slightly harder resin.

The total combined monomer level had to be adjusted to between 25-35% to permit ready wet out of the fiberglass mat or fabric. Lower amounts of monomer caused difficulties in the wet out of fiberglass with vinyl ester resins. Therefore, the monomer combinations to be considered were styrene, vinyl toluene, vinyl toluene/ 1,4-butanediol diacrylate, and vinyl toluene/hydroxypropyl methacrylate. The primary criteria for selecting any of these combinations or even to look for another was adhesion, which depended on the lap shear results.

Several other acrylate monomers which were evaluated as possible modifiers for the vinyl ester resin formulations are listed in Table 23. The 1,6-hexanediol diacrylate could be substituted for the 1,4-butanediol diacrylate if we need to speed up the slower resin or increase the hardness. The polyurethane diacrylate might be used as an adhesion promoter and improve elongation if needed.

TABLE 23

EVALUATION OF OTHER MONOMERS FOR POSSIBLE USE IN THE REPAIR PATCH

Monomer	%Initiator	Time to T_{max}	T_{max}, °F	Barcol	Comments
1,6-hexanediol diacrylate	0.4	1.1	478		almost too reactive verybrittle
" "	0.6	1.5	474		"
isobornyl acrylate	0.4	4.2	265		
Ebecryl 4830 (aliphatic polyurethane diacrylate)	0.4	7.2	261		tacky

Cargill 1574 base stock resin was selected as the primary backup resin for the special vinyl novolac that Cargill manufactured for us in their pilot plant. Formulation work with either resin is directly applicable to both resins. The advantage of using these base stock resins was that we could vary the monomer and the amount of monomer to optimize the resulting formulation for both the putty component and the actual prepreg patch.

Table 24 lists the results of various formulation and evaluation runs with 1574. These results showed that the use of the less volatile vinyl toluene in place of styrene gave the same cure rate and a higher Barcol. In fact, the reduction of monomer down to 15% (0.4% photoinitiator) actually increased the rate of cure without a decrease in Barcol. However, the increased viscosity at these lower monomer levels was a disadvantage. The cure rate for the 100% base stock resin significantly slowed down while also giving a lower Barcol. Hydroxypropyl methacrylate(HPMA) was also examined as another less volatile monomer. It had much the same effect as the vinyl toluene with slightly higher Barcols. The vinyl toluene gives lower shrinkage, while the HPMA gives better adhesion especially in high humidity situations. The corresponding hydroxypropyl acrylate(HPA) gave lower Barcols as expected.

It was decided to use the base resin(1574) and the primary selected resin (1721)at 80% with 20% monomer to minimize the amount of monomer without sacrificing properties and cure rate. The 20% monomer is a blend of the less volatile monomers, vinyl toluene and the HPMA, in order to minimize volatility when the patch was used in confined situations. The HPMA was included to maximize adhesion and Barcol. The rate of cure for these various blends was usually less than three minutes which was satisfactory. The optimum rate of cure occurred with 10% of each of these monomers and 80% 1574 base stock resin. If we need to decrease viscosity, we will just add more of the 50-50 blend of vinyl toluene-HPMA. The reduction of monomer content and the use of substantially less volatile monomers as compared to styrene make fabrication and patching with this system inside vehicles safer and far less bothersome.

Evaluation of the optimum photoinitiator level indicated that with this resin blend, we should use 0.3% instead of 0.4% although the system is not particularly sensitive to excess photoinitiator. In fact the system did not appear to be very sensitive to excess hydroquinone or acrylic acid, two materials which could accidently vary in concentration depending on manufacturing conditions.

This resin blend (80% 1574 or 1721, 10% vinyl toluene, and 10% HPMA) was very satisfactory at this point for the actual field repair patch.

TABLE 24
EVALUATION OF CARGILL 1574 BASE STOCK WITH VARIOUS MONOMERS
(0.4% Photoinitiator)

Monomer %			Time to T_{max}	T_{max}°F	Barcol
60	styrene	40	4.3	289	40-42
65	"	35	2.9	270	42-44
55	vinyl toluene	45	4.0	275	44-46
60	"	40	4.3	270	44-46
65	"	35	3.2	263	44-46
70	"	30	3.0	269	44-46
80	"	20	2.6	243	48-50
80	"	20	3.1	188	50
	(0.6% photoinitiator)				
85	"	15	2.4	208	50
100%	pure base stock resin		5.0	180	42-44
55	hydroxypropyl methacrylate(HMPA)	45	2.5	235	42-44
60	"	40	2.6	232	42-44
70	"	30	3.1	253	46-48
80	"	20	2.7	220	48-50
85	"	15	2.9	204	48-50
60	vinyl toluene(VT) HPMA	15 25	2.6	249	48-50

TABLE 24 (CON'T)

60	"	15	2.2	226	42-44
	hydroxypropyl acrylate(HPA)	25			
60	"	25	4.0	277	42-44
	HPA	15			
80;	VT 10;	HMPA 10	2.7	223	48-50
80;	VT 10;	HMPA 10	2.5	233	48-50
	(0.2% photoinitiator)				
80;	VT 10;	HMPA 10	2.3	190	47-49
	(0.3% photoinitiator)				
80;	VT 10;	HMPA 10	2.9	189	48-50
	(0.5% photoinitiator)				
80;	VT 10;	HMPA 10	2.8	222	48-50
	(0.6% photoinitiator)				
80;	VT 10;	HMPA 10	3.8	203	49
	(1.0% photoinitiator)				
65;	VT 15;	HMPA 20	3.2	212	44
70;	VT 10;	HMPA 20	2.9	188	43
65;	VT 15;	HPA 20	2.9	238	40
80;	VT 10;	HMPA 10	2.9	208	46-48
	(0.05% hydroquinone added)				
80;	VT 10:	HMPA 10	2.7	225	46-48
	(1.0% acrylic acid added)				

A series of runs were made to evaluate the effect of styrene separately and combining vinyl toluene(VT) and hydroxypropyl methacrylate(HPMA) on the cure rate and Barcol with 1721 resin as compared to 1574. The results were similar and are listed in Table 25. The Time to T_{max} was 2.4-3.1 minutes with 20-35% combined monomers and 0.3-0.4% photoinitiator which was as expected. The Barcols ranged from about 40 to 50 with a >44 desired. The work with 1574 as the base stock resin and 411-35 as an additional backup resin(only available with styrene) correlated directly with the results from the scaled up vinyl acrylated epoxy novolac.

It was important to minimize the monomer percentage(<30%) and to try to eliminate styrene in these compositions since people will be using these patches in a wide variety of situations including closed interiors. At the same time, we did not want to sacrifice physical properties, cure rate, and adhesion.

TABLE 25
EVALUATION OF SCALED UP VINYL ACRYLATED EPOXY NOVOLAC

Resin%	Additive%	PI%	Time to T_{max}	T_{max},°F	Barcol	Comments
65	styrene 65	0.2	3.7	294	44	
"	"	0.3	3.2	314	49	
"	"	0.4	3.1	332	50	
"	"	0.5	3.3	297	48	
"	"	0.6	3.7	260	42	
80	VT(10);HPMA(10)	0.4	3.3	214	40	
70	(15); (15)	"	2.5	240	42	
65	(10); (25)	"	2.8	239	49	

The evaluation of this vinyl epoxy novolac with glass fabric from Vetrotex^r or E glass fabric from Fiber Glass Industries in a four-ply form(woven roving, mat, woven roving, mat) gave excellent cure time results in the sun. The cure times with the release film still on the patch were less than two minutes to a hard surface. (Note that the surface will be tacky if the release film is removed prior to curing.) The monomers that were selected are hydroxypropyl methacrylate and vinyl toluene at 20-25% combined level. (Alternatively styrene can be interchanged with the vinyl toluene.) This completed the blended resin development phase for this program.

The tensile strength of the resin mixture used for the patches was determined to be 11,500 psi with 7% elongation. The heat deflection temperature is expected to be over 300°F. This resin ranks with the epoxies, and it should have better hot wet strength.

Cargill informed us that drum quantities will constitute commercialization and that this was a new resin. We have submitted a Preliminary Manufacturing Notice to the EPA for this resin which has been approved.

Storage Stability and Inhibitors. In order to maximize shelf life, particularly under worst case conditions, stability studies with varying amounts of inhibitor were run with Derakane 411-45 (a methacrylated vinyl BPA resin with styrene). It was found that the maximum addition of inhibitor over the amount of inhibitor (estimated 0.02-0.08 %) already in the resin mix was 0.2%. It was found that the addition of higher amounts of inhibitor (0.4% or more) significantly slowed the cure rate (twice as long) and lowered the Barcol dramatically to about 0. Several naphthahydroquinones, hydroquinone, and toluhydroquinone were surveyed. Hydroquinone appeared to have the least effect on the Barcol of the inhibitors at the 0.2% level. Samples of 411-45 containing no additional inhibitor, 0.1% additional inhibitor, and 0.2% additional inhibitor were impregnated into glass mat and sealed in aluminized pouches and placed into an oven at 140°F. These samples were checked for stiffness every day. The uninhibited samples became stiff after 2 days. The 0.2% inhibited sample became stiff after seven days. Normally in a desert climate without any protection one would not expect the temperature to be at 140°F for more than four hours a day. This would mean that unprotected storage might be about six weeks with 0.2% inhibitor with Derakane 411-45.

Additional high temperature prepreg storage tests showed that 0.1 % hydroquinone added to an unsaturated ortho ester Silmar (S4A) and to a vinyl BPA ester (Interplastic VE 8750) maintained the sealed fiberglass prepreg satisfactorily flexible and tacky for seven weeks at 140° F. This should be equivalent to at least eight months (assuming four hours a day physically at 140° F) in a desert climate if not in direct sunlight.

The uncured impregnated patch containing the selected resin(1721) in a sealed aluminum pouch was determined to be stable at 140°F for longer than three weeks with 0.1% hydroquinone added. This would be about eight months in a desert climate.

A.2.4. Optimization of Resin Adhesion and Adhesive Putty Development

Initially the adhesion of the photocured resins against different surfaces was measured to see what improvement was needed. Various techniques and additives were then examined to see how much effect these had. An optimum solution then evolved from this work. The primary means for determining the relative adhesion of the different bonding to surfaces was the use of lap shear determinations.

Adhesion Studies. The sample preparation for the lap shear testing was performed by overlapping a coupon of the test surface and a coupon of the uncured prepreg and then curing the prepreg directly on the test surface. Great care was needed to achieve good alignment or the results would be low. These test specimens were placed directly into the tensile tester (Instron) and the lap shear measured at break. Initially, it was difficult to achieve consistent values until the laboratory technique for carefully aligning the samples before and during photocure of the prepreg against the other surface was perfected.

A layer of 24-oz E-glass woven roving with nonwoven fiberglass mat at the interface filled with Derakane 411-45 was cured as one patch onto the surface of a previously cured coupon of the same composition. The lap shear average of seven determinations throwing out the highest and lowest values was 1742 lbs/sq.in. The failure mode was cohesive in all samples and some glass fiber pull out was noted from the fabric yarn. Although the technique developed for sample preparation was not exactly the ASTM procedure because of the need to photocure the resin patch from one side, the results were consistent on a comparative basis. These results can be compared with results obtained with other lap shear techniques. This lap shear of 1742 lbs/sq.in. compared favorably with values of 1000 to 3000 lbs/sq.in. for lap shears of adhesive bonds reported for other thermoset resin systems which are considered satisfactory to exceptional. The cohesive failure mode which was found showed that the lap shear value in these cases was resin limited and that the interfaces of the two surfaces were satisfactorily fusing or bonding. Samples were held 24-hours before testing.

Further lap shear tests with Derakane 411-45 against aluminum were conducted. Priming the aluminum surface with 1% Z-6026(a Dow Corning aminotrimethoxy silane) in isopropanol increased the lap shear to over 1600 psi. One percent by weight of this primer was incorporated into the bottom layer of the patch to see if this could eliminate the adhesion problem, and the need for a separate priming step. (Although even without the primer, the lap shear with aluminum was in excess of 1100 psi with no additives and quite satisfactory.) Table 26 lists lap shear determinations of the vinyl ester novolac 1721 with 35% styrene and Derakane 411-45.

TABLE 26
LAP SHEAR RESULTS FOR FIBERGLASS/RESIN CURED AGAINST VARIOUS SURFACES

Resin	Surface	Conditions	Lap Shear, lbs/sq.in.
411-45	aluminum	clean surface	1100 (previous result)
"	steel	" "	1030
"	aluminum	2% amino silane in resin of bottom mat layer	1912
"	"	1% " " "	1529
"	steel	2% " " "	1372
"	"	1% " " "	1127
vinyl ester novolac (158-1721-69)	aluminum	clean surface	994
"	steel	" "	1073
"	aluminum	2% amino silane in resin of bottom layer	1865

We had established a goal to improve the lap shear from about 1000-1100 psi to above 1800 with both aluminum and steel. (The lap shear results for resin against resin were already above this 1800 psi level.) At this point, 1% aminosilane in isopropanol when used as a surface primer on the metal gave results above 1880 psi for both of the resins on aluminum. It also increased the lap shear for 411 on steel to 1855 psi for Derakane 411 and to 1376 psi for the new vinyl novolac resin. When 2% aminosilane primer was incorporated instead into the bottom layer of the patch, lap shears over 1800 psi were achieved for aluminum with both resins. Using the same approach, the lap shears for steel were 1300-1400 psi for both resins. The use of 2% acrylic acid in the bottom patch layer did not make a significant difference over the unprimed patch. The best way to utilize these adhesion promoters was to put them into the bottom layer of the patch or into a putty which would be used anyway to prepare a smoother surface for the repair patch. This latter approach was the preferred one since the putty was already part of the repair kit.

Additional lap shear testing showed that an acrylated urethane oligomer will also provide improved bonding to metals. When a rigid acrylated polyurethane(Sartomer 9706) with 15% styrene (for improving the flowability) was used as the resin in the bottom patch layer, the lap shear for Derakane 411-45 against aluminum was 1830 psi and against steel it was 1050 psi. Replacing 9706 with a more elastic acrylated polyurethane incorporating 35% styrene produced lap shears of 1982 psi against aluminum and 1372 psi against steel. (In the cases of lap shear tests against metals, the metal surface is always lightly sanded.) Either the aminosilane (N-{3-[trimethoxysilyl]-propyl}ethylene diamine) or the polyurethane interface will work as satisfactory adhesion promoters against metals for these vinyl ester systems. Therefore we concluded that one of these promoters would be included into the repair system.

Since we decided to include a putty as a side pouch with the patch for smoothing the surface and filling in holes, incorporate the adhesion promotor would be included in the putty. In this way the putty would be applied as a thin layer over the entire area to be patched. The repair patch would then be applied to this tacky surface. The process of applying the putty would actually improve the wet out of the dusty or possibly still dirty surface to be repaired, and improve or simplify surface preparation. Older FRP surfaces tend to be dusty and a light sanding is helpful for improving the "bite" of the new resin layer to be added.

The problem is to keep the surface preparation to the minimum necessary for the requirement. For the fastest repair with simple sealing required, just put the patch into place and cure. If structural integrity and reinforcement are a concern, then the surface should be lightly sanded and wiped clean with a solvent.

Because of the importance of the putty, the physical properties of the putty needed to be optimized and the adhesion promoters needed to be incorporated. Previously the putty had served to be more of a good filler to obtain smoother surfaces for the patch. The putty had included acrylic resin (PMMA) dissolved in hydroxypropyl methacrylate, styrene and an unsaturated isophthalate ester resin. The PMMA was eliminated and a vinyl ester resin included as the structural resin with a mix of hydroxypropyl acrylate or methacrylate and vinyl toluene along with the adhesion promoter. A small amount of an organic diisocyanate was used to reactively crosslink the resin oligomers which provides the necessary thickening of the putty along with presence of chopped fiberglass or other ceramic thixotropic agent. The hydroxypropyl acrylate or methacrylate provides enough compatibility with water to permit ready clean up with water, good bonding, and good toleration of a damp surface. The changes were made stepwise so as to determine the specific formulation problems as they occurred. The use of 25% Derakane 411-25 as the resin backbone gave Time to T_{max} of 4.9 minutes with 0.4% photoinitiator which compared favorably with a simple binary mix of 25% PMMA and 75% hydroxypropyl methacrylate which was 5.0 minutes.

The use of the adhesion promoted putty appeared to be the simplest approach for a general purpose field repair patch for all surfaces and most requirements.

The 1574 blended vinyl ester resin and 411-35 vinyl ester resin were found to be good starting points for the thickened putty. This included the addition of glass fiber and a ceramic fiber. We also tried to obtain low shrinkage on curing which enhances adhesion.

The important criteria for the putty was that: 1) it is thick enough yet is flowable with the 10-15% contained chopped glass fiber; 2) it truly gives good adhesion against most if not all surfaces; 3) it cures at a satisfactory rate. Table 28 lists the lap shear results for putties made from 80% 1574 with 10% HPMA and 10%VT and thickened with 2-4% FiberFrax and 8-10% fiberglass. Lap shear results are also given for 411-35 putties for comparison. (We found that we did not need additional thickening with the organic diisocyanate in the case of the putty.) These putties contained 2% aminosilane as the adhesion promotion agent. The lap shear was done with precured patch plates and with the patch and putty cured all at the same time against aluminum and steel. The surfaces were always lightly sanded with sand paper. The bond between the putty and the patch always held. The bond between the metal surfaces and the cured resin broke sometimes adhesively and sometimes cohesively which was also a good sign. The adhesion to the metal surfaces under these conditions was satisfactory with lap shears above 1050 psi for steel and above 1400 psi for aluminum. Additionally, good lap shear results were also obtained without the aminosilane /putty against aluminum. We believe that the putty will always be the preferred way to put on the patch. These results are listed in Table 27. However, the adhesion of these cured resins was good against aluminum without the aminosilane. The adhesion to steel is the critical factor in determining which adhesion promoter to use.

TABLE 27
LAP SHEAR RESULTS FOR PUTTY FORMULATION

(80% resin; 2% aminosilane: 20% HMPA: 2% FiberFrax; 10% chopped glass; 0.4% PI)

Putty Resin Base	Patch Plate	Surface	Lap Shear, PSI
411-35	411-35	steel	1246
411-35	precured 411-35	steel	1372
none	411-35 (No aminosilane)	aluminum	1097
411-35	precured 411-35	aluminum	1522
411-35	411-35	aluminum	1340
(1574 Putty: 80% 1574; 105 HMPA; 10% VT; 2% aminosilane; 2% Fiber Frax; 10% fiber glass; 0.3% PI)			
1574	precured 411-35	steel	1050
1574	411-35	aluminum	1440
none	1574 (no aminosilane)	aluminum	1425
none	1721 (no amino silane)	aluminum	1696

The adhesion against steel varied from 570 psi with no aminosilane primer present in the putty up to 1625 psi for 2% aminosilane present as the primer with Derakane 411 based putties. For instance, 0.5% aminosilane present gave about 1200 psi and 1.0% gave 1400 psi. The adhesion against aluminum ranged from 800 psi with no aminosilane primer to 1900 psi with 2% aminosilane primer in putty.

The putties based on Derakane 411 thickened severely over several days in the presence of the aminosilane primer.

The use of the diacrylated polyurethane at the 20% level in the putty showed no improvement over the standard Derakane 411-35 putty which had no aminosilane primer included. (The aminosilane still caused the 411-45 putty composition to slowly gel over a week even at 1% loading.) The use of a methacrylic trimethoxysilane also offered no improvement in adhesion against steel as compared with the plain putty.

Therefore we evaluated other resins for the basic putty resin as to whether they would thicken when containing the aminosilane promoter. Such a resin was found. A commercial maleic anhydride /propylene glycol unsaturated polyester resin with 2% aminosilane primer in this resin putty did not cause thickening or gelling even at 140°F for week. The adhesion against steel was very good with a lap shear over 1700 psi. The lap shear against aluminum was over 2000 psi for this same putty. We finally had found a satisfactory putty to promote adhesion for the field repair patch.

A.2.6. Design and Fabrication of Ten Portable UV Lamps Which Function on 24-V Vehicle Battery

Photolamp Development. Initially, we had to determine what the configuration and specifications for the field repair light should be for a photocure lamp for field repair use. The initial photocure lamps that were evaluated were:

Spectronics 100-watt flood lamps (2types)
Spectronics 125-watt spot lamps (2 types)
Spectronics "Supercharger" 100-watt/135-watt SPR 100C; best of this group
Dr. Honle 200-watt hand held 220-Volt unit
Dr. Honle 400-watt fixed unit. (This is the unit which we used in the laboratory since it approximated sunlight at 12 inches distance from the resin surface.)

In order to obtain the best unit for this application, various manufacturers of these types of bulbs were contacted. We discussed with different UV lamp manufacturers their ability to build a ruggedized bulb and mounting fixture at a reasonable price.

The development of the portable UV Lamp was planned to proceed as follows:

I. Define the light intensity requirements.
   A. Patch cure speed requirement
      1. 5-10 minute cure
      2. 3-5 minute cure time
      3. 1-3 minute cure time.

- B. Stray light problems
  - 1. Threat of identifying a target to opposing forces
  - 2. Shielding requirements for personnel (flash blind).

II. Define design modifications necessary for field deployment
- A. Design of lamp
- B. Design of housing
- C. Design of power supply
- D. Determine design of total package.

The design criteria for the portable light was worked out based on minimizing weight, cost, and keeping the cure time under ten minutes for up to a 10" x 10" patch.

Design Criteria For Photocure Lamp

1. The lamp must have sufficient power to photocure the repair patch at the same rate as sunlight or faster. (Under ten minutes with a 0.25-in thick patch.) This means the lamp output in the UV_a region would be sufficient for this task.

2. The peak power available will be a 200 amps at 24 Volts D.C.

3. The area of cure for the photocure lamp will be a minimum of 6"x 6" square.

4. The lamp assembly with a 20-foot cord without the case should be as light as possible, preferably under eight pounds.

5. The lamp should be as rugged as possible.

6. The lamp should not put out excessive heat so that it can be used in the interior of a vehicle with the crew in it.

7. The lamp housing should be protective and convenient to place over the patch or to hand hold in place.

8. The cost should be kept to the lowest possible when made in volume.

9. The total assembly in the case with patches should take up the minimum volume of space.

This list narrowed down the choice of lamps and actual designs dramatically. The type of UV_a lamps that were available were:

1) Actinic: Spectral distribution does not fall mainly within the 370-410nm range. No further consideration of this lamp.

2) Metal Halide: The appropriately modified metal halide lamp has a favorable spectral energy distribution. The Sylvania Metalarc Clear lamp is a ruggedized lamp and available in sizes from 175 watts and up. This is an arc tube lamp and not a flood type of lamp. These lamps operate at several atmospheres pressure internally and can be a potential hazard. These lamps would probably be the best choice for a fixed installation, but not for a field lamp selected for a lightweight and minimum power system with maximum safety.

3) Spectral: These lamps currently do not exceed 90 watts and appear to be too small.

4) Sun: These lamps are a variation on the mercury vapor lamp which will be discussed below. As an example, the RS Sun lamp is a 275-watt, self-ballasted mercury lamp with a built in reflector.

5) Super Diazo Blue Fluorescent: This lamp spectral output has its peak at 420nm with most of its energy output above 410nm. This is not the desired range for our application.

6) Mercury Vapor: The mercury vapor lamp is the most common and readily available source of UV energy. Sylvania mercury vapor lamps were all originally designed for outdoor use. Consequently, all of their mercury vapor lamps have been ruggedized with the exception of the PAR(parabolic aluminized reflector)lamps. The Sylvania clear mercury vapor lamp has the highest UV output of the mercury vapor lamps in the desired region. This is the lamp being supplied by Spectronics as the SPR 100 both in a spot and a flood version.

The necessary type of lamp for the UV, photocure was either a metal halide mercury vapor lamp or a mercury vapor lamp because of the efficiency in the desired wavelength range (365-410 nm). The metal halide lamp is far more delicate and generates 20-30 pounds internal pressure during use. Additionally, it runs a lot hotter than the mercury vapor lamp which is considered a low temperature lamp. For these reasons we selected the mercury vapor lamp. We also decided to use a flood lamp as opposed to a spot beam because of the necessity of photocuring a larger area (>6"x6"). These lamps run on AC current and require significant voltage.

The total components for the lamp assembly were the lamp, the ballast, the transformer, and the invertor conversion. We consolidated these functions into two components, the bulb and everything else through use of a solid state designed combined balast/transformer/inverter.

The type and power output of the UV bulb determines the power requirements and the weight of the electrical package that must accompany the bulb. Therefore it was important to pick the best practical bulb from the point of view of efficiency, lowest wattage needed, and overall size while considering ruggedness, cost, and commercial availability. It appeared that a 100-watt lamp is the optimum size lamp from the electrical package point of view. At this level of power the necessary inverter and transformer can readily be combined using solid state electronics to give a component weighing only a few pounds. Power requirements over 100 watts would not be able to utilize the solid state electronics needed to make a compact integrated unit and the weight and cost increased disproportionately and significantly above this power level. The selection of a 100-watt bulb as the size to focus on in the development permitted the weight of the total package to be kept under ten pounds.

The mercury vapor lamp (SPR 100) was chosen as the initial candidate lamp because of its availability, ruggedness, spectral range, relative efficiency, and price. Preliminary testing of the effectiveness of a 100-watt mercury vapor lamp for photocuring a patch was done using this SPR 100 lamp with a Spectronics holder and transformer and with Derakane 411-45 as the model resin. The results of this testing are given in Table 28. Both spot (focused) and flood lamp versions of the SPR-100 were used. Both of these lamps have a supercharge mode which increases the power to the light, but cuts down on the life of the bulb. As the distance from the light(outer protective filter) to the resin surface is increased, the area irradiated increases, but the energy striking the resin surface decreases. Initially, we simply compared the 100-watt bulb at three inches with our standard light(400-watt metal halide at 12 inches) which we have used all along for our resin development. Since the 100-watt bulb at 3 inches was much faster than the reference, the distance was increased to 6 inches which also gave an irradiated area of about 6 in. x 6 in. The cure time was still faster than the reference.

The 100-watt mercury vapor bulb was the smallest size that would be satisfactory. The baselining of the bulb permitted the other lamp components to be configured and obtained.

TABLE 28
EFFECT OF PHOTOLAMPS ON CURING DERAKANE 411-45 RESIN
(0.4% photoinitiator)

UV Lamp	Conditions	Distance;in.	Time to T_{max}	T_{max}°C	Barcol	Comments
Reference standard for this series		12	4.7	244	40	dry cure
1.SPR 100 Flood; Spectronics	normal mode	3	3.2	320	40	"
2. "	"	6	4.4	305	40	"
3. "	" (<360nm filter removed)	6	4.0	303	40	"
4. "	super charge mode	3	3.0	350	40	"
5. "	"	6	3.9	281	40	"
6. "	" (<360nm filter removed)	6	3.8	280	40	"
7. SPR 100 Spot; Spectronics	normal mode	3	3.7	286	40	"
8. "	super charge mode	3	3.5	390	40	"

Investigation of power supplies. Five companies confirmed that they would design and build a mil. spec. prototype combined inverter/transformer for the 100-watt lamp with a 24-Volt, 200-amp DC power source(battery). Of these, three were in the $2-3,000 range and were nearby which was necessary for ready access to the lights:

1) Centerset, Inc.;
2) Magnetic Design Labs, Inc.; and
3) LESCO, Inc.

Centerset, Inc. was selected for the design and fabrication of the combined inverter/transformer for the 100-watt mercury vapor lamp. This configuration weighed less than two pounds. This meant that the total assembly would weigh significantly under ten pounds, easily meeting our weight goal. A breadboard model of the proposed field UV$_a$ lamp was evaluated before locking in this particular configuration. After that breadboard showed no sign of design problems, we placed the order for the specially designed prototype ballast/inverter /transformer.

A 24-Volt portable gel battery pack was connected to a DC inverter and 100-watt mercury vapor lamp as a breadboard mock up of the proposed field repair lamp system. The initial UV mercury vapor lamp which was used had a spot focus. The lamp was positioned ten inches above a 411-45/fiberglass prepreg and curing time noted. The prepreg cured in five minutes in an area which was 6" x 6" although the center of the patch cured even faster. When the lamp was raised to fifteen inches above the surface, the cure time increased to 5.8 minutes and the cured area was 9" x 9".

A flood lamp of the same power achieved a larger area at the same distances without sacrificing cure rate. Evaluation of the 100-watt photoflood lamp in the bread board mock up of the lightweight field UV light was done with Derakane 411-45. At 14 inches from the surface of the glass/resin prepreg (4 plies), a 9-inch diameter circle was cured in 12 minutes. At 21 inches from the surface, a 12-inch diameter circle was cured in 15 minutes. This convinced us that the 100-watt lamp was sufficient to meet our original goals for field repair curing. This enabled us to keep the supporting electrical package lighter in weight.

The initial circuit designed for the combined ballast/ inverter/ transformer for the 100-watt photoflood lamp was found to overheat and cut out. The second design did accomplish the desired curing of a standard patch at 10 inches, but required a 20-minute warm up time. A third circuit modification was evaluated with a photoflood lamp. At 12 inches from the surface, the patch(411-45) cured in 5 minutes at center and required 31 minutes to cure a 12" x 12" area. At 17.5 inches from the surface, the patch required 5 minutes to cure at its center and 17 minutes to cure a 12" x 12" area. At 25" inches from the surface, the patch required 7 minutes to cure at its center and 25 minutes to cure a 12" x 12" area. The difficulty was that we were operating on a 24-Volt DC source, and we wanted the electronics to be lightweight. This made an unusual requirement from a circuit design point of view. (We did not have the final vinyl novolac resin at this time to do these evaluations.)

The light cured vinyl novolac resin patch cured in a 12-inch circle in 5 minutes at 14 inches from the surface. The bulb used was a Spectronics 100-watt flood. (Sunlight cures the same patch in about 2-3 minutes depending on the time of day.)

A set of twelve boards was ordered based on this successful board. These boards were incorporated into an aluminum container for the first time to give the prototype units. The parts of the unit were based on the best industrial components available since none of the mil. spec. parts were available in this small of a quantity. This prototype unit met all the goals set for it including weight reduction and size. Further reduction in size and weight will depend on a large production order which would justify the appropriate manufacturing tooling. The completed units were found not to overheat even when left on for several hours. tI was also decided that the system would function on 21-28 Volts only to avoid draining down the battery of a vehicle too much for it to start on this same battery.

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