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**DEVELOPMENT OF A TRANSPARENT ADHESIVE
COMPATIBLE WITH POLYCARBONATE
FOR USE IN BALLISTIC SHIELDS**

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G.L. Ball III
I.O. Salyer

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Technical Report AFML-TR-70-144

June 1970

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DEVELOPMENT OF A TRANSPARENT ADHESIVE COMPATIBLE
WITH POLYCARBONATE FOR USE IN BALLISTIC SHIELDS

G. L. Ball III
I. O. Salyer

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MRC-DA-256

FOREWORD

This project was carried out in the Polymer Applications Section of the Dayton Laboratory of Monsanto Research Corporation, Dayton, Ohio, under Air Force Contract F33615-69-C-1190.

This contract was initiated under Project Number 7381, "Materials Application," Task 738108. "Application of Materials and Processes for Tactical Warfare." This program is administered by the Air Force Materials Laboratory, Air Force Systems Command, Wright-Patterson Air Force Base, with Mr. R. E. Wittman as Project Engineer.

This work was conducted under the technical direction of Mr. I. O. Salyer. Mr. G. L. Ball III was Project Leader and the Principal Investigator, and was assisted by Mr. R. D. Myers and Mr. T. J. Bucher.

This report describes work performed from 1 June 1969 to 31 March 1970.

Acknowledgment is given to Monsanto Company and to Libbey-Owens Ford Company for their support in supplying some necessary materials at no cost to the program.

This technical report has been reviewed and is approved.

Albert Olevitch

Albert Olevitch, Chief
Materials Engineering Branch
Materials Support Division
Air Force Materials Laboratory

ABSTRACT

The use of polycarbonate in transparent ballistic shields has been severely hampered by the lack of availability of suitable adhesives. In particular the thermoplastic adhesives which have had more prominence in the past are not compatible with polycarbonate. Some thermosetting materials have been made available, but these too are limited due to inherent fabrication problems and sensitivity to moisture. The improved toughness of polycarbonate over acrylic, however, is sufficient to warrant the development of a suitable thermoplastic adhesive.

A series of proprietary ethylene terpolymer compositions were made available by Monsanto Research Corporation. In a very limited experimental program it was shown that at least one of these compositions was found to be entirely satisfactory for bonding glass to polycarbonate. In addition to the polycarbonate compatibility, the advantages of this adhesive are that (1) it provides excellent and controllable adhesion to various glasses and polycarbonate, (2) it is elastomeric and stable over a broad temperature range, (3) it can be made crystal clear, (4) the modulus characteristics can be adjusted without the inclusion of a plasticizer, (5) the material is a thermoplastic and therefore can be handled with standard autoclaving techniques, and (6) the material potentially can be made available at a relatively low cost.

It was demonstrated that glass-polycarbonate laminates bonded with the ethylene terpolymer could withstand repeated thermal cycling from -60°F to $+140^{\circ}\text{F}$. Thus the potential for using this in unheated aircraft windshields was indicated. While not conclusively demonstrated, it was shown that the thermal cyclic stability could be increased to $+165^{\circ}\text{F}$ and probably higher. Ballistic tests at velocities up to 1500 feet per second confirm the excellent bond strength of this adhesive to both polycarbonate and glass.

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SECTION I

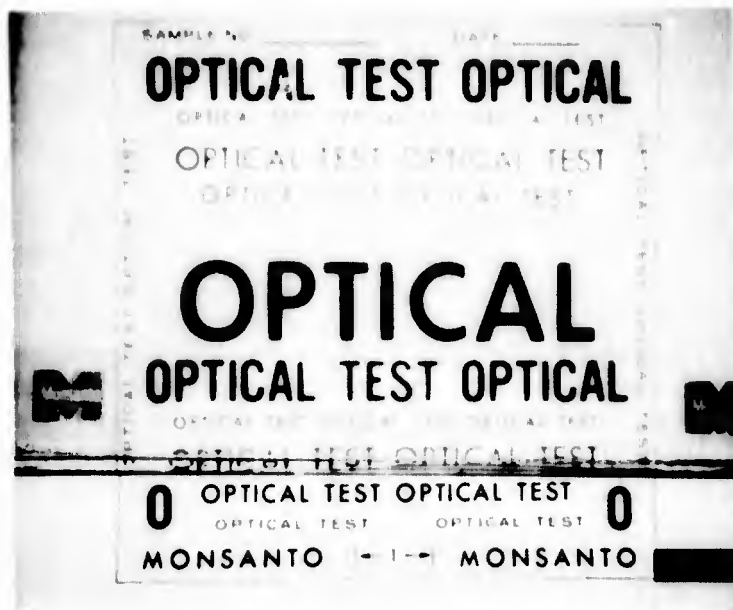
INTRODUCTION

Transparent armor is an important military item used to maintain the usefulness of military aircraft and vehicles. In most combat situations there is a necessity for direct visual observation by personnel using vehicles and aircraft and a need to protect these personnel from injury and critical components from malfunction. Owing to the critical need for transparent armor in Southeast Asia, vastly improved transparent materials have been developed and made available through various research programs.

The best present transparent ballistic shields consist of various combinations of high strength glass, tough polycarbonate or acrylic plastic, and transparent adhesives for bonding these together into laminates of desired thicknesses. Major improvements in the strength and hardness of available glasses and the clarity of polycarbonate have occurred which make them the most suitable materials for the ballistic shield application. Polyvinylbutyral (PVB), a proven transparent adhesive through many years of use in automobile and aircraft transparent safety shields, continues to provide an effective means for bonding various layers of glass together. Attempts at modifying polyvinylbutyral, however, to render it suitable for use with polycarbonate have been less than satisfactory (Ref. 1). At best, the present PVB introduces haze into a polycarbonate laminate as is demonstrated in Figure 1.

Cast-in-place urethanes have been made available for bonding polycarbonate to glass, and this material circumvents the compatibility problem of the PVB. There are two major problems with the cast-in-place urethane, however, which make it a much less than desirable solution to the bonding problem. First of all, techniques for casting in place to bond together two transparent plates are unsatisfactory. A good bond layer can be accomplished only with meticulous care to provide for the removal of bubbles and to account for shrinkage during polymerization. Second, polyurethanes are highly sensitive to moisture, and this property inhibits the ready fabrication of a haze-free adhesive layer and can result in debonding at the urethane-glass or urethane-polycarbonate surface of a laminate.

As a means of circumventing the problems of these transparent adhesives for bonding glass to polycarbonate, Monsanto Research Corporation made available a proprietary series of materials based on an ethylene polymer. These materials were most attractive since they were compatible with polycarbonate (being internally plasticized), were not sensitive to moisture or water and were



0° Obliquity



45° Obliquity

Figure 1. Glass-Polycarbonate Laminate Bonded With A Modified Polyvinylbutyral Showing The Problem Of Haze.

thermoplastic and therefore could be handled in the same manner as PVB. These proprietary materials were also elastomeric and thus it was anticipated that they could withstand the stresses introduced due to the considerably different thermal coefficients of expansion of the glass and polycarbonate.

The objectives of the program conducted, therefore, were to (1) produce transparent laminates consisting of glass, polycarbonate, and the various ethylene terpolymers; (2) to evaluate these systems, compared to other existing systems, in terms of optical clarity, adhesion, and stability from -65°F to $+165^{\circ}\text{F}$ and (3) to characterize the ethylene terpolymers to the extent required for this particular application. This series of ethylene terpolymers consisted of nine compositions which were considered to encompass the characteristics required for the laminating application. Only a very limited amount of material was available, however, and therefore it was required that a detailed and step-by-step screening program be conducted to eliminate the less interesting compositions toward providing the one or two best candidates.

The experimental program was designed to prove that the ethylene terpolymer adhesive was adequate and to demonstrate its utility by a very limited number of tests. Adhesive availability would not allow the preparation of quantities of transparent laminates for a statistical ballistic characterization or for other long-term and large-scale studies.

SECTION II

SUMMARY AND CONCLUSIONS

Through a designed experimental program involving nine ethylene terpolymer compositions, a range of adhesive strengths and rigidities most applicable to the glass-polycarbonate system were defined. Four more promising materials, each which could be rated as best for a given temperature-performance region, resulted. Finally, the most promising composition, based on thermal cycling data on glass-polycarbonate laminates was determined.

The thermal-modulus characteristics of the four more promising compositions developed are shown in Figure 2. Each of the compositions differed in hydroxyl content as indicated in the figure. For these particular materials, as hydroxyl content was increased (which provides for greater adhesive bonding to both the polycarbonate and the glass), the rigidity of the adhesive also increased. For the bonding application this was in the direction opposite to that which is most desirable. Ideally, a highly extensible elastomeric material with maximum adhesive characteristics is preferred.

In this particular system, compromise and therefore optimization, was required. It was shown that this optimum combination of properties could be achieved. A summary of the parameters from the curves shown in Figure 2, as well as some additional data on mechanical strength, elongation and impact, are shown in Table I. The increase in tensile strength, adhesive shear strength, toughness (impact), and a corresponding decrease in percent elongation as the hydroxyl content of the composition increases are shown.

Using the four best compositions, and especially the composition containing 3.5% hydroxyl (identified as 35772-3,0), the various glass-polycarbonate laminates were physically characterized. The results were best described qualitatively through photographs of the particular laminates. The optical clarity of this adhesive was demonstrated and is shown in Figure 3. Two laminates are shown: that on the left consisted of two pieces of glass bonded together with the adhesive (3.5% OH); that on the right was two pieces of polycarbonate. Clarity and freedom from haze are shown to be excellent and any decrease in transparency was attributed to the polycarbonate. Naturally, the compatibility with polycarbonate was also demonstrated here.

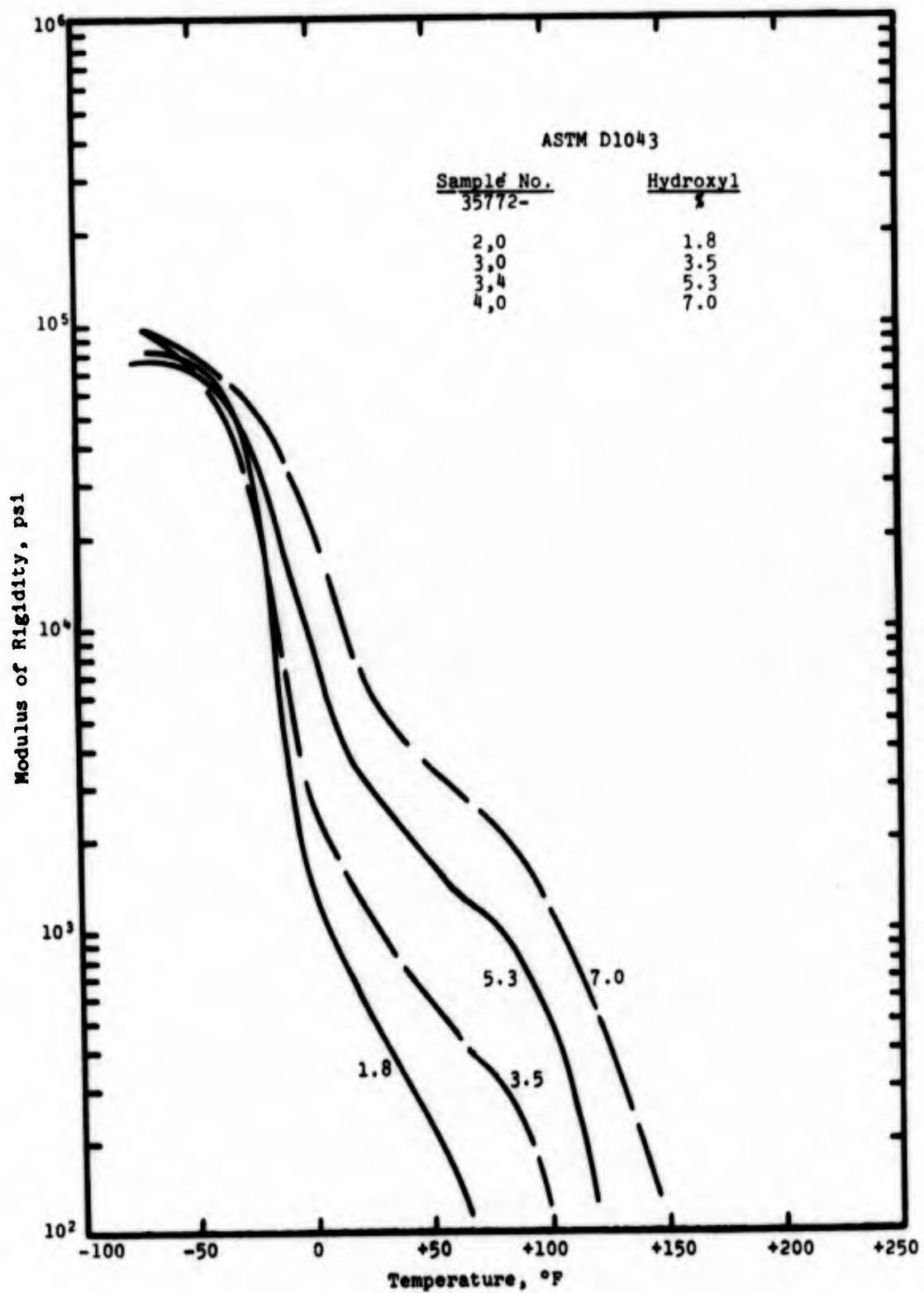


Figure 2. Thermal-Modulus Characteristics of the Four More Promising Terpolymers.

Table I

SUMMARIZED MECHANICAL CHARACTERISTICS OF THE
ETHYLENE TERPOLYMERS AS RELATED TO HYDROXYL CONTENT

| Sample I.D. No. (35772-) | Hydroxyl Content (%) | Impact Tensile ¹ (ft lb/in.) | Tensile ² Strength (psi) | Elongation (%) | Tf (°F) | Modulus of Rigidity ³ T ₆₇₅ (°F) | SR (°F) | Lap ⁴ Shear Strength (psi) |
|-----------------------------|----------------------|---|-------------------------------------|----------------|---------|--|---------|---------------------------------------|
| 2,0 | 1.8 | 530 | 360 | >600 | -30 | +15 | 45 | 320 |
| 3,0 | 3.5 | 860 | 590 | >600 | -35 | +40 | 75 | 370 |
| 3,4 | 5.3 | - | 2000 | 1100 | -25 | +90 | 115 | 230 |
| 4,0 | 7.0 | 1150 | 1140 | 170 | -20 | +115 | 135 | 870 |

¹ASTM D1822 - Rate = 11 ft/sec.

²ASTM D638 - Rate = 0.05 to 20 in./min.

³ASTM D1043 - Tf = temperature at modulus of 45,000.

T₆₇₅ = temperature at modulus of 675.

SR = T₆₇₅ - Tf, (Stiflex Range).

⁴ASTM D1006 - Rate = 0.05 in./min, 23°C 100% adhesive failures.

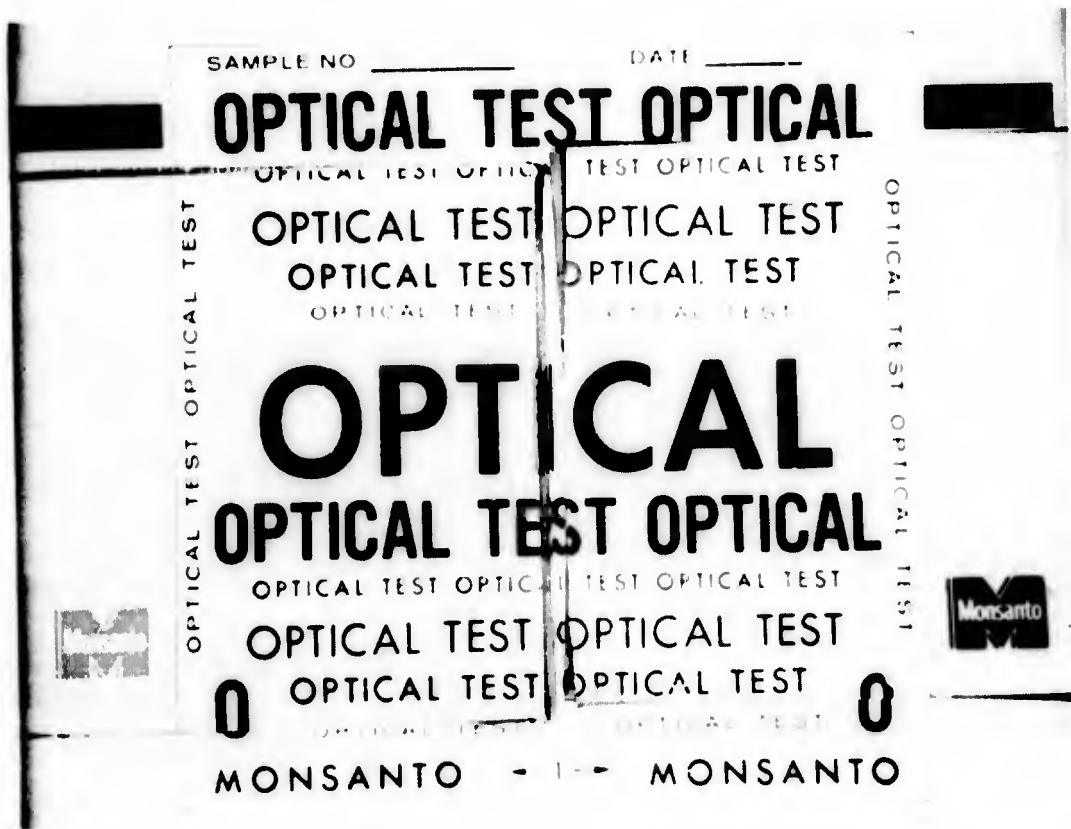


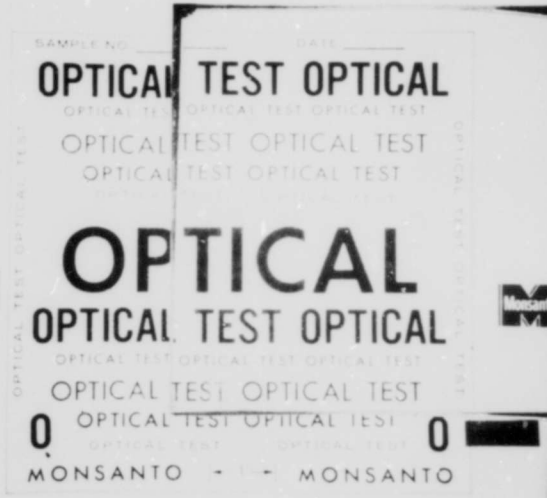
Figure 3. Two Pieces Of Glass (left) And Polycarbonate (right) Bonded Together With 3.5% OH Ethylene Terpolymer.

Figure 4 shows some additional qualities of the adhesive. First of all, this is a glass-polycarbonate laminate and therefore the compatibility of the adhesive with the polycarbonate was again demonstrated. Second, the glass used was aluminum borosilicate high-strength glass and the bond to it was therefore demonstrated. Third, in using the total one-inch thick laminate, the freedom from distortion and the excellent optical characteristics of this system were demonstrated and are shown by the photographs taken at both 0° and 45° obliquity.

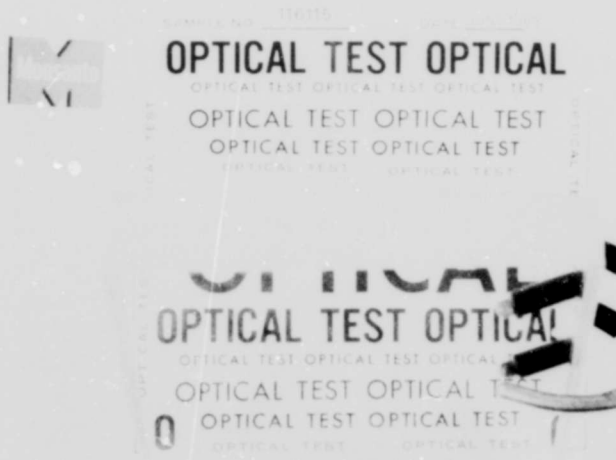
Most important were the bonding characteristics of the adhesives. These qualities were demonstrated in photographs taken following various characterization tests. Figure 5 shows glass-polycarbonate systems that had received ballistic impacts. The top photograph in Figure 5 shows a soda lime glass-polycarbonate laminate which had been impacted with a 17-grain fragment simulator. Of importance is the fact that, even though fracture occurred, transparency in the unfractured regions was maintained. Thus, adhesion to both the glass and the polycarbonate was maintained. Indeed, the only fracture that occurred was in the glass itself; a thin layer of glass remained bonded to the polycarbonate after the ballistic tests.

A number of tests were performed to demonstrate the ability of this adhesive to maintain bonding throughout thermal cycling. The most representative results were indicated by a thermal shock and repeated thermal cycling test series. In the thermal shock experiment, two pieces of soda lime glass were bonded with 20 mils of the adhesive (3.5% OH). This laminate was immersed directly from room temperature into a -65°F silicone bath, was soaked for ten minutes, and then was directly immersed into a +180°F bath where it was soaked for an additional ten minutes. The laminate maintained its integrity throughout this thermal shock (however, it would not be expected to hold up under repeated thermal shocks of this nature).

More realistic and representative of the efficacy of this system was the stability of a few glass-polycarbonate laminates which were bonded together with 20 mils of the adhesive (3.5% OH). These withstood 36 thermal cycles from -65°F to +135°F and an additional 18 thermal cycles from -65°F to +140°F. These elastomeric properties of the ethylene terpolymers at low temperature provide a basis for considering this material as a potential for aircraft windshield interlayers. The advantage over present materials is that electrical heating may not be required. The need for deicing equipment (conductive coating type heaters), however, would not be eliminated.

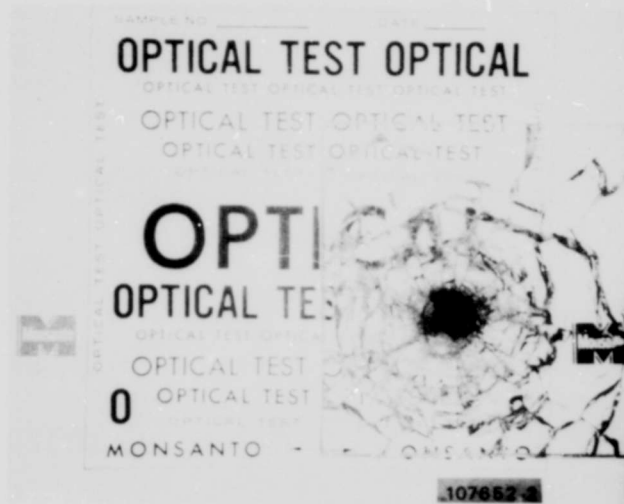


0° Obliquity



45° Obliquity

Figure 4. Aluminum Borosilicate Glass-Polycarbonate Laminate Bonded with 3.5% OH Ethylene Terpolymer.



(a) Soda Lime Glass Impacted With 17 Grain 0.222 Caliber Fragment At 1000 Ft. Per Second.



(b) Aluminum Borosilicate Glass Impacted with Caliber .30 AP Projectile At 1500 Ft. Per Second.

Figure 5. Glass-Polycarbonate Laminates Broken By Ballistic Impact.

The only limitation of the system shown was some lack of integrity in the neighborhood of +150°F to +165°F. While the mechanism was not confirmed, it was felt that too high a degree of softening of the adhesive occurred, allowing separation and the formation of bubbles within the laminate. One way of correcting this limitation is to slightly crosslink the polymer adhesive. This would increase its form stability at the higher temperatures. We were not able to optimize this degree of crosslinking. The feasibility of this approach was demonstrated, however, and we were able to increase form stability (as demonstrated by an increase in zero tensile strength) by at least 40°F.

SECTION III

EXPERIMENTAL DISCUSSION

Our experimental program to elucidate the efficacy of the ethylene terpolymer adhesive as a bonding medium for glass and polycarbonate consisted of the following four primary tasks:

- (1) Thermal mechanical screening of the ethylene terpolymer adhesives;
- (2) Physical characterization of the ethylene terpolymer adhesives;
- (3) Preparation of laminates incorporating the ethylene terpolymer adhesive; and
- (4) Physical characterization of the transparent laminates.

Because of the very limited amount of adhesive material available for the program, it was necessary that the major portion of the work be conducted on the first two tasks to screen out the less interesting compositions. Of interest was the definition of four candidates for characterization in laminates in the third and fourth tasks. Also, due to the limited program, it was necessary that characterization of the transparent laminates be primarily on a qualitative rather than quantitative basis. Toward meeting the objectives of the program, this was not at all objectionable and indeed was most rewarding.

1. THERMO-MECHANICAL SCREENING OF THE ETHYLENE TERPOLYMER ADHESIVES

Nine ethylene terpolymer adhesive compositions (proprietary) were evaluated. These consisted of an ethylene polymer series in which the hydroxyl content was varied. The hydroxyl content ranged from 1.8 to 9.5%.

A complete characterization of all nine of these compositions was not provided for. They therefore were screened to provide the four most promising or representative. The screening was conducted by thermo-mechanical characterization of the adhesives using the Clash-Berg modulus technique (ASTMD-1043). The results of the Clash-Berg tests were curves representing the modulus of rigidity (psi) as a function of temperature (°F).

The importance of the thermo-mechanical analysis was a determination of the modulus of the compositions at their temperature extremes, especially at -65°F and $+165^{\circ}\text{F}$, and the determination of the rate at which this modulus changed as a function of temperature. The elasticity of the adhesive at the various temperatures would thus be known and a relative measure of the toughness of the system could be inferred by the breadth and magnitude of the temperature-modulus curves.

Sample identification, their hydroxyl content, and the Clash-Berg temperatures corresponding to specific moduli are shown in Table II.

The complete modulus-temperature curves for the nine adhesive compositions are shown in Figure 6. The curves shown in Figure 6 demonstrate the increased breadth of the temperature transition region as the hydroxyl content is increased. This fact was also demonstrated by the last column in Table II, which shows the Stiflex Range (SR) for each composition. The Stiflex Range is the temperature over which the modulus of the polymer decreases from 45,000 to 675 psi.

Based on the modulus-temperature characteristics and to a lesser extent on the availability of the particular composition, four materials were selected for further study. The particular adhesives were those containing 1.8, 3.5, 5.3, and 7.0% OH. Their modulus-temperature characteristics were shown earlier in Figure 2.

2. PHYSICAL CHARACTERIZATION OF THE ETHYLENE TERPOLYMER ADHESIVES

To provide a basis for selecting the best adhesive compositions for a given application, and to provide engineering parameters for use in the design of transparencies, a short study to determine the mechanical properties of the bulk adhesives alone was conducted.

Tensile strength and elongation, tensile impact, and lap shear strengths were measured. The thermo-mechanical characteristics described in Section I were also significant for this purpose. The results of these tests are shown in Table II.

All tests were conducted at 23°C (74°F) and 50% RH using ASTM standard methods. The tensile impact was conducted at 11 ft/sec using a pendulum-type impactor, and the tensile strengths and elongations were conducted at rates from 0.5 to 20 in/min on an Instron tensile tester. Lap shear adhesion was determined on 1 inch wide aluminum coupons.

The results shown in Table I indicate the direct relationship between tensile impact, tensile strength, and adhesive strength with hydroxyl content, and the inverse relationship between percent elongation and hydroxyl content. The direct relationship between tensile impact and Stiflex range is also shown in Table II.

Table II
MECHANICAL AND THERMOMECHANICAL CHARACTERISTICS
OF THE ETHYLENE TERPOLYMERS AS A FUNCTION OF HYDROXYL CONTENT

| Sample I.D. No. (35772-) | Selected | Hydroxyl Content (%) | Impact Tensile ¹ (ft lb/in.) | Tensile ² | | Modulus of Rigidity ³ | | Lap Shear Strength (psi) | |
|--------------------------------|----------|----------------------------|---|----------------------|-------------------|----------------------------------|--------------------------|--------------------------------|------------|
| | | | | Strength (psi) | Elongation (%) | T _f (°F) | T ₆₇₅ (°F) | | SR (%F) |
| 2,0 | X | 1.8 | 530 | 360 | >600 | -30 | +15 | 45 | 320 |
| 2,3 | | 2.7 | - | - | - | -35 | +30 | 65 | |
| 3,0 | X | 3.5 | 860 | 590 | >600 | -35 | +40 | 75 | 370 |
| 2,4 | | 4.4 | - | - | - | -30 | +65 | 95 | |
| 3,4 | X | 5.3 | 78 | 2000 | 1100 | -25 | +90 | 115 | 230 |
| 2,5 | | 5.6 | - | - | - | -45 | +100 | 145 | |
| 4,0 | X | 7.0 | 1150 | 1140 | 170 | -20 | +115 | 135 | 870 |
| 4,5 | | 8.2 | - | - | - | -15 | +130 | 145 | |
| 5,0 | | 9.5 | 1310 | 2230 | 400 | +5 | +160 | 165 | |

¹ASTM D1822 - Rate = 11 ft/sec.

²ASTM D638 - Rate = 0.05 to 20 in./min.

³ASTM D1043 - T_f = temperature at modulus of 45,000.
T₆₇₅ = temperature at modulus of 675.
SR = T₆₇₅ - T_f, (Stiflex Range).

⁴ASTM D1006 - Rate = 0.05 in./min, 23°C, 100% adhesive failures, refer to NSP 116199.

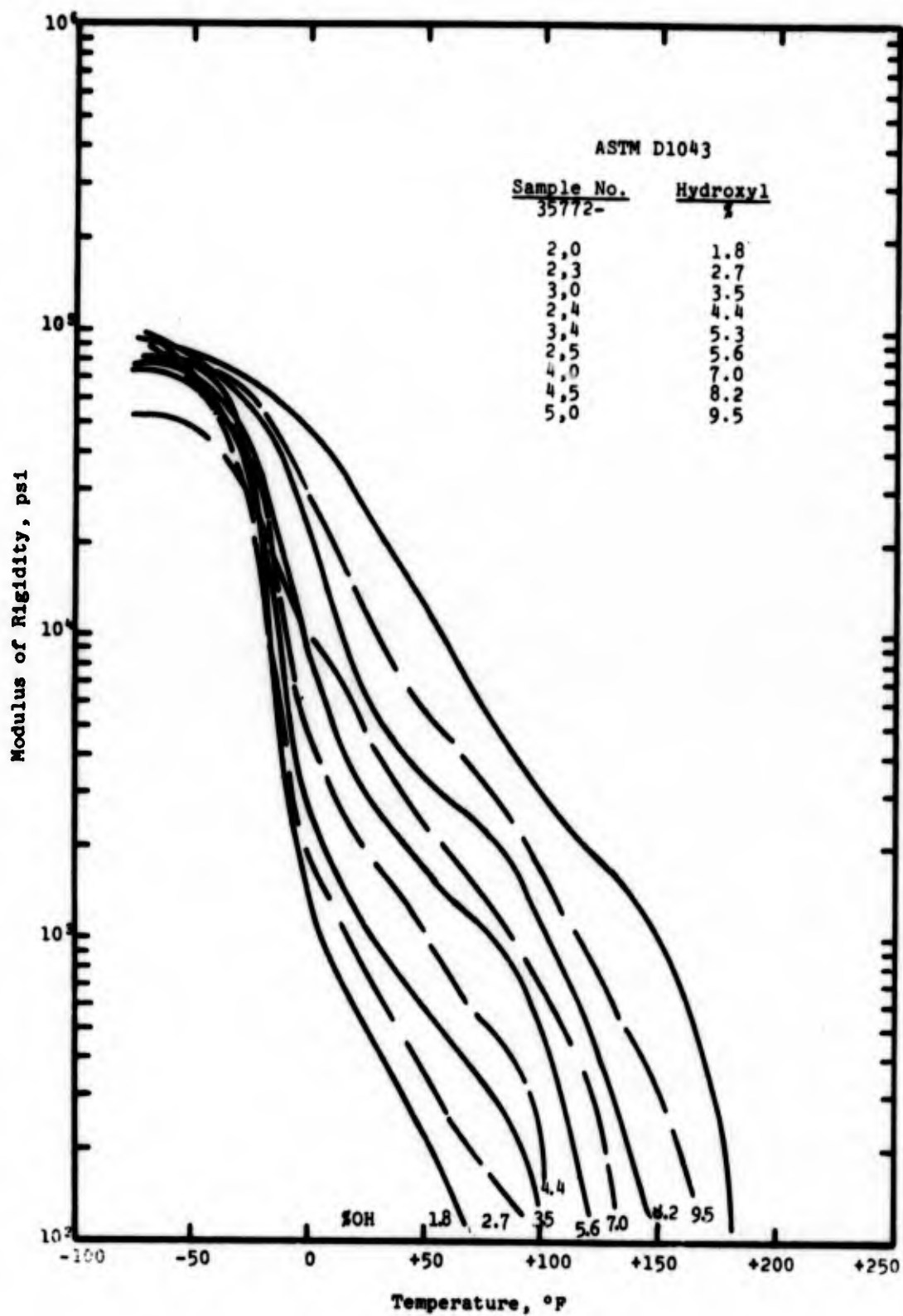


Figure 6. Modulus of Rigidity as a Function of Temperature for the Nine Ethylene Terpolymers Investigated.

3. PREPARATION OF TRANSPARENT TEST LAMINATES

To demonstrate the efficacy of the various ethylene terpolymer adhesive compositions, laminates consisting of glass-polycarbonate, glass-glass, and polycarbonate-polycarbonate, were prepared. A standard polyvinylbutyral and a modified polyvinylbutyral bonded laminate was also fabricated in order to demonstrate the problem and the degree of success achieved.

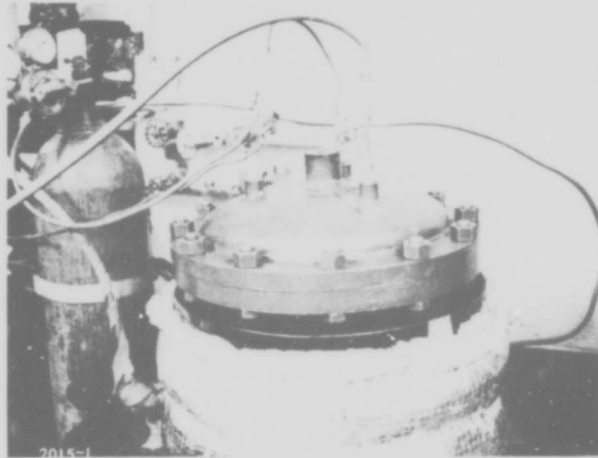
The laminates were prepared in an air-type autoclave, which is shown in Figure 7. The technique used is similar to that for bonding materials with polyvinylbutyral. It involved elevated temperature- and pressure-bonding of the transparent plates in the autoclave. Each composite structure was first laid up and sealed within an aluminized Mylar bag on which a vacuum was maintained throughout the entire autoclaving cycle. This provided for removal of all volatiles.

The heating was achieved through an exterior oil bath and the pressure provided through a cylinder of nitrogen. With this equipment temperatures of up to 300°F and pressures of up to 150 psi could be achieved. In most instances, temperatures of up to 250°F and pressures of 15 psi were used. No major effort was expended on determining the best laminating conditions. Thus we were conservative and just used a temperature-pressure cycle of heating to +250°F in three hours followed by cooling to room temperature overnight. The vacuum was maintained on the bag and a pressure of 15 psi on the autoclave throughout the entire thermal cycle.

Importantly, also, the glass and polycarbonate were all routinely cleaned with appropriate solvents, acids, and detergents solutions before use. Following any cleaning procedure, the specimens were also dried in a moderately elevated temperature oven. The adhesives were dried too, but this was done only as an extra precaution, and probably was not required.

The laminates that were prepared are detailed in Tables III, IV and V. These tables give the identification number of the laminate, the type and thickness of adhesive used, the total number of non-adhesive plies in the laminate, the number of plies of polycarbonate and glass, and the dimensions of the flat surface of the laminate. These tables also contain comments regarding the laminates. These comments are discussed in Section IV.

Table III describes the laminates that consisted of a single ply each of glass and polycarbonate. The ethylene polymers having 1.8, 3.5, 5.3, and 7.0% OH were used to bond these laminates together. The laminates listed in Table IV all consisted of two plies of soda lime glass and were bonded with the same ethylene terpolymer compositions as those shown in Table III.



(a) Autoclave and Associated Equipment.



(b) Mylar Bagged Laminate (Vacuum Port Attached).

Figure 7. Equipment for Pressure-Vacuum Laminating.

Table III
COMPOSITION AND CHARACTERISTICS OF GLASS-POLYCARBONATE
LAMINATES PREPARED FOR OPTICAL AND MECHANICAL EVALUATION

| Sample No. | Adhesive ¹ code (No.) | Adhesive ² Thickness (mils) | Total Plies | Glass Plies | Glass Thickness (Inches) | PC ³ Plies | PC Thickness (Inches) | Laminate ⁴ Dimensions (Inches) | Laminate ⁵ Condition | Shock ⁶ Cycles (No.) | Thermal ⁷ Cycles -65 to +165°F (No.) | Thermal ⁸ Cycles -65 to +130 (No.) | Remarks ⁹ | Photo ¹⁰ |
|------------|----------------------------------|--|-------------|-------------|--------------------------|-----------------------|-----------------------|---|---------------------------------|---------------------------------|---|---|----------------------|---------------------|
| 161-1 | 2 | 10 | 2 | 1 | .250 | 1 | .250 | 5x5 | GOOD | | | | LSS ALSO | |
| 644-2 | 2 | 20 | 2 | 1 | .250 | 1 | .250 | 5x5 | GOOD | | | | REFORM | |
| 121-3 | 2 | 20 | 2 | 1 | .250 | 1 | .250 | 5x5 | GOOD | | | | LSS ALSO | |
| 161-2 | 2 | 20 | 2 | 1 | .250 | 1 | .250 | 5x5 | GOOD | F1 | | | | |
| 195-1 | 2 | 20 | 2 | 1 | .250 | 1 | .250 | 5x5 | | | | | 9 CYCLES | |
| 945-1 | 2 | 20 | 2 | 1 | .250 | 1 | .250 | 5x5 | GOOD | F1 | | | REFORM | |
| 121-4 | 2 | 30 | 2 | 1 | .250 | 1 | .250 | 5x5 | GOOD | | | | | |
| 673-1 | 3 | 10 | 2 | 1 | .250 | 1 | .250 | 5x5 | GOOD | | | | LSS ALSO | X |
| 162-1 | 3 | 10 | 2 | 1 | .250 | 1 | .250 | 5x5 | GOOD | | | | LSS ALSO | X |
| 649-2 | 3 | 20 | 2 | 1 | .250 | 1 | .250 | 5x5 | FAIR | P1 | | | | X |
| 652-2 | 3 | 20 | 2 | 1 | .250 | 1 | .250 | 5x5 | FAIR | P1 | | | 650FS IMP | X |
| 654-2 | 3 | 20 | 2 | 1 | .250 | 1 | .250 | 5x5 | | | | | | |
| 674-2 | 3 | 20 | 2 | 1 | .250 | 1 | .250 | 5x5 | POOR | | | | CRACKED | |
| 676-3 | 3 | 20 | 2 | 1 | .250 | 1 | .250 | 5x5 | GOOD | | | | | |
| 901-1 | 3 | 20 | 2 | 1 | .250 | 1 | .250 | 5x5 | GOOD | | | | REFORM | |
| 121-5 | 3 | 20 | 2 | 1 | .250 | 1 | .250 | 5x5 | GOOD | | | | LSS ALSO | |
| 162-2 | 3 | 20 | 2 | 1 | .250 | 1 | .250 | 5x5 | GOOD | | | | 9 CYCLES | |
| 924-1 | 3 | 20 | 2 | 1 | .250 | 1 | .250 | 5x5 | GOOD | F1 | | | | X |
| 117-2 | 3 | 30 | 2 | 1 | .250 | 1 | .250 | 5x5 | GOOD | | | | | |
| 121-6 | 3 | 30 | 2 | 1 | .250 | 1 | .250 | 5x5 | FAIR | | | | BR BUBL | |
| 974-1 | 3 | 30 | 2 | 1 | .250 | 1 | .250 | 5x5 | EXCL | | 36 | | | |
| 974-2 | 3 | 30 | 2 | 1 | .250 | 1 | .250 | 5x5 | EXCL | | 36 | | 18 TO 140 | |
| 975-3 | 3 | 30 | 2 | 1 | .250 | 1 | .250 | 5x5 | GOOD | | 15 | | XLNK GF | |
| 979-3 | 3 | 30 | 2 | 1 | .250 | 1 | .250 | 5x5 | GOOD | | 18 | | XLNK GF | |
| 674-3 | 3 | 30 | 2 | 1 | .250 | 1 | .250 | 5x5 | POOR | | | | CRACKED | |
| 676-1 | 3 | 30 | 2 | 1 | .250 | 1 | .250 | 5x5 | EXCL | P2 | | | | X |
| 163-1 | 34 | 10 | 2 | 1 | .250 | 1 | .250 | 5x5 | GOOD | | | | HAZE LSS | |
| 644-3 | 34 | 20 | 2 | 1 | .250 | 1 | .250 | 5x5 | GOOD | | | | HAZE | |
| 164-2 | 34 | 20 | 2 | 1 | .250 | 1 | .250 | 5x5 | GOOD | | | | HAZE LSS | |
| 936-1 | 34 | 20 | 2 | 1 | .250 | 1 | .250 | 5x5 | | | | | | |
| 929-1 | 34 | 20 | 2 | 1 | .250 | 1 | .250 | 5x5 | POOR | | | | HUBL | |
| 944-1 | 34 | 20 | 2 | 1 | .250 | 1 | .250 | 5x5 | FAIR | F1 | | | BUBL | |
| 642-1 | 4 | 20 | 2 | 1 | .250 | 1 | .250 | 4x5 | POOR | | | | CRACKED | |
| 121-7 | 4 | 20 | 2 | 1 | .250 | 1 | .250 | 5x5 | POOR | | | | DEBUD ZJA | |
| 141-1 | 4 | 20 | 2 | 1 | .250 | 1 | .250 | 5x5 | FAIR | | | | FLAME PC | |
| 924-5 | 4 | 20 | 2 | 1 | .250 | 1 | .250 | 5x5 | POOR | | | | | |
| 925-1 | 4 | 20 | 2 | 1 | .250 | 1 | .250 | 5x5 | | | | | | |
| 944-4 | 4 | 20 | 2 | 1 | .250 | 1 | .250 | 5x5 | POOR | | | | HUBL | |
| 941-3 | 4 | 20 | 2 | 1 | .250 | 1 | .250 | 5x5 | POOR | | | | | |
| 945-1 | 4 | 20 | 2 | 1 | .250 | 1 | .250 | 5x5 | GOOD | | | | | |
| 662-1 | 4 | 30 | 2 | 1 | .250 | 1 | .250 | 5x5 | POOR | | | | DEBUD-PC | |
| 679-1 | 4 | 30 | 2 | 1 | .250 | 1 | .250 | 5x5 | FAIR | P1 | | | DEBUD | |
| 121-8 | 4 | 30 | 2 | 1 | .250 | 1 | .250 | 5x5 | POOR | | | | DEBUD | |
| 688-2 | 4 | 40 | 2 | 1 | .250 | 1 | .250 | 5x5 | POOR | | | | | |
| 679-2 | 4 | 40 | 2 | 1 | .250 | 1 | .250 | 5x5 | POOR | | | | | |
| 640-3 | 4 | 60 | 2 | 1 | .250 | 1 | .250 | 5x5 | POOR | | | | CRACKED | |
| 674-3 | 4 | 60 | 2 | 1 | .250 | 1 | .250 | 5x5 | POOR | | | | DEBUD | |

¹2 is 1.8% OH, 3 is 3.5% OH, 34 is 5.4% OH, and 4 is 7.0% OH containing ethylene terpolymer.
²Does not include adhesive layer.
³PC - Polycarbonate.
⁴Front Surface.
⁵Based on visual inspection of clarity, freedom from haze, bubbles and unbonded sections.
⁶Shock cycle consisted of direct immersion into -65°F liquid and transfer to +180°F liquid.
⁷Passed with no visible change.
⁸Thermal Cycle: 74°F to 165°F for 15 minutes, hold at 165°F for 4.5 hours, cool to -65°F in 15 minutes, hold at -65°F for 1 hour, equilibrate to 74°F (RT) in 2 hours.
⁹* Indicates number of cycles required to cause visible failure.
¹⁰Thermal Cycle: Same as indicated in footnote ⁸ except upper temperature was 130°F.
¹¹LSS- Lap shear specimen prepared; reform- laminated second time to eliminate imperfections;
¹²IMP- Ballistic impact tested at speed shown; 18 to 140- number of thermal cycles to +140°F;
¹³XLNK- crosslinked; Flame PC- flame treated °C; NR- no bond, SB- some bond.
¹⁴Photograph taken for record.

Table IV
COMPOSITION AND CHARACTERISTICS OF GLASS-GLASS
LAMINATES PREPARED FOR OPTICAL AND MECHANICAL EVALUATION

| Sample No. | Adhesive ¹ Code (No.) | Adhesive ² Thickness (mils) | Total Plies | Glass Plies | Glass Thickness (Inches) | PC ³ Plies | PC Thickness (Inches) | Laminate ⁴ Dimensions (Inches) | Laminate ⁵ Condition | Shock ⁶ Cycles (No.) | Thermal ⁷ Cycles | Thermal ⁸ Cycles | Remarks ⁹ | Photo ¹⁰ |
|------------|----------------------------------|--|-------------|-------------|--------------------------|-----------------------|-----------------------|---|---------------------------------|---------------------------------|-----------------------------|-----------------------------|----------------------|---------------------|
| | | | | | | | | | | | -65 to +165°F (No.) | -65 to +130 (No.) | | |
| 681-1 | 2 | 20 | 2 | 2 | .250 | 0 | | 5x5 | EXCL | | | | RW | |
| 150-1 | 2 | 20 | 2 | 2 | .250 | 0 | | 5x5 | GOOD | | F1 | | | |
| 195-2 | 2 | 20 | 2 | 2 | .250 | 0 | | 5x5 | | | | | | |
| 230-2 | 2 | 20 | 2 | 2 | .250 | 0 | | 5x5 | GOOD | | F1 | | | |
| 157-2 | 2 | 30 | 2 | 2 | .250 | 0 | | 5x5 | GOOD | | F1 | | | |
| 933-0 | 2 | 40 | 2 | 2 | .250 | 0 | | 5x5 | GOOD | | | | TC IN LAM | |
| 649-1 | 3 | 20 | 2 | 2 | .250 | 0 | | 5x5 | FAIR | | | | RW BUHL | |
| 652-1 | 3 | 20 | 2 | 2 | .250 | 0 | | 5x5 | FAIR | P1 | | | 650FS IMP | X |
| 654-1 | 3 | 20 | 2 | 2 | .250 | 0 | | 5x5 | | | | | | |
| 931-2 | 3 | 20 | 2 | 2 | .250 | 0 | | 5x5 | | | | | | |
| 157-3 | 3 | 20 | 2 | 2 | .250 | 0 | | 5x5 | GOOD | | F1 | | | |
| 151-0 | 3 | 20 | 2 | 2 | .250 | 0 | | 5x5 | POOR | | | | NO BAG BHL | |
| 928-2 | 3 | 20 | 2 | 2 | .250 | 0 | | 5x5 | GOOD | | F1 | | | |
| 953-2 | 3 | 20 | 2 | 2 | .250 | 0 | | 5x5 | GOOD | | | | | |
| 117-1 | 3 | 30 | 2 | 2 | .250 | 0 | | 5x5 | EXCL | | | | | X |
| 150-4 | 3 | 30 | 2 | 2 | .250 | 0 | | 5x5 | GOOD | | F1 | | | |
| 153-1 | 34 | 20 | 2 | 2 | .250 | 0 | | 5x5 | GOOD | | F1 | | HAZE | |
| 934-2 | 34 | 20 | 2 | 2 | .250 | 0 | | 5x5 | | | | | | |
| 929-2 | 34 | 20 | 2 | 2 | .250 | 0 | | 5x5 | FAIR | | | | | |
| 944-2 | 34 | 20 | 2 | 2 | .250 | 0 | | 5x5 | FAIR | | 9 | | | |
| 153-2 | 34 | 30 | 2 | 2 | .250 | 0 | | 5x5 | GOOD | | | | HAZE | |
| 642-2 | 4 | 20 | 2 | 2 | .250 | 0 | | 4x5 | POOR | | | | GLS FRCT | X |
| 153-3 | 4 | 20 | 2 | 2 | .250 | 0 | | 5x5 | FAIR | | F1 | | | |
| 191-2 | 4 | 20 | 2 | 2 | .250 | 0 | | 5x5 | FAIR | | | | CLN GLASS | |
| 925-2 | 4 | 20 | 2 | 2 | .250 | 0 | | 5x5 | FAIR | | F1 | | | |
| 153-4 | 4 | 30 | 2 | 2 | .250 | 0 | | 5x5 | GOOD | | | | | |

¹2 is 1.8% OH, 3 is 3.5% OH, 34 is 5.3% OH, and 4 is 7.0% OH containing ethylene terpolymer.
²Does not include adhesive layer.
³PC - Polycarbonate.
⁴Front Surface.
⁵Based on visual inspection of clarity, freedom from haze, bubbles and unbonded sections.
⁶Shock cycle consisted of direct immersion into -65°F liquid and transfer to +180°F liquid.
⁷Passed with no visible change.
⁸Thermal Cycle: 74°F to 165°F or 15 minutes, hold at 165°F for 4.5 hours, cool to -65°F in 15 minutes, hold at -65°F for 1 hour, equilibrate to 74°F (RT) in 2 hours.
⁹- indicates number of cycles required to cause visible failure.
¹⁰Thermal Cycle: Same as indicated in footnote ⁷ except upper temperature was 130°F.
¹¹BH - Sample delivered to R. E. Wittman for inspection; TC IN LAM - thermocouple laminated in for temperature measurement; NO BAG - Sample not bagged for laminating;
¹²CLN Glass - glass surface cleaned three times.
¹³Photograph taken for record.

Table V

COMPOSITION AND CHARACTERISTICS OF MISCELLANEOUS
EXPLORATORY LAMINATES PREPARED FOR OPTICAL AND MECHANICAL EVALUATION

| Sample No. | Adhesive ¹ Code (No.) | Adhesive ² Thickness (mils) | Total Glass | | Glass Thickness (Inches) | PC ³ Files | PC Thickness (Inches) | Laminate ⁴ Dimensions (Inches) | Laminate ⁵ Condition | Shock ⁶ Cycles (No.) | Thermal ⁷ Cycles | Thermal ⁸ Cycles | Remarks ⁹ | Photo ¹⁰ |
|------------|----------------------------------|--|-------------|-------|--------------------------|-----------------------|-----------------------|---|---------------------------------|---------------------------------|-----------------------------|-----------------------------|----------------------|---------------------|
| | | | Files | Files | | | | | | | -65 to +165°F (No.) | -65 to +130 (No.) | | |
| 681-3 | 2 | 20 | 2 | 0 | | 2 | .250 | 5X5 | GOOD | | | | | |
| 676-2 | 3 | 30 | 2 | 0 | | 2 | .250 | 5X5 | GOOD | | | | | |
| 674-0 | 4 | 30 | 2 | 0 | | 2 | .250 | 5X5 | GOOD | | | | RW | |
| 686-0 | 3 | 20 | 2 | 1 | .250 | 1 | .250 | 6X6 | GOOD | | | | RW HSG | |
| 690-0 | 3 | 20 | 2 | 2 | .250 | 0 | | 6X6 | GOOD | | | | HSG | X |
| 115-0 | 3 | 30 | 2 | 1 | .500 | 1 | .500 | 6X6 | EXCL | | | | HSG | X |
| 112-0 | 3 | 30 | 2 | 1 | .500 | 1 | .500 | 6X6 | EXCL | | | | HSG 1500AP | X |
| 699-0 | 3 | 30 | 2 | 2 | .250 | | | 0X1 | GOOD | | | | | X |
| 696-0 | 3 | 20 | 2 | 1 | .500 | 1 | .500 | 0X1 | EXCL | | | | | |
| 923-1 | VB | 20 | 2 | 1 | .250 | 1 | .250 | 5X5 | POOR | | | | HIGH HAZE | X |
| 923-2 | VB | 20 | 2 | 2 | .250 | 0 | | 5X5 | EXCL | | | | MOD PVB | |
| 923-3 | FX | 25 | 2 | 1 | .250 | 1 | .250 | 5X5 | POOR | | | | CRAZED | |
| 923-4 | FX | 25 | 2 | 2 | .250 | 0 | | 5X5 | EXCL | | | | STD PVB | |

¹ 2 is 1.85 OH, 3 is 1.55 OH, 3a is 5.35 OH, and 4 is 7.05 OH containing ethylene terpolymer.

² Does not include adhesive layer.

³ PC - Polycarbonate.

⁴ Front Surface.

⁵ Based on visual inspection of clarity, freedom from haze, bubbles and unbonded sections.

⁶ Shock cycle consisted of direct immersion into -65°F liquid and transfer to +180°F liquid.

⁷ P - passed with no visible change.

⁸ Thermal Cycle: 74°F to 165°F for 15 minutes, hold at 165°F for 4.5 hours, cool to -65°F

in 15 minutes, hold at -65°F for 1 hour, equilibrate to 74°F (RT) in 2 hours.

⁹ RW - indicates number of cycles required to cause visible failure.

¹⁰ Thermal Cycle: Same as indicated in footnote ⁷ except upper temperature was 130°F.

¹¹ RW - Sample delivered to R. E. Wittman for inspection; HSG - PPG Aluminum Borosilicate glass

¹² #7428; MOD PVB; unmodified PVB; STD PVB - standard grade PVB for safety glass.

¹³ Photograph taken for record.

Table V lists some miscellaneous laminates that were prepared for the program for various purposes. They included the bonding of two pieces of polycarbonate; the use of PPG aluminum borosilicate glass; the fabrication of a 10 inch x 10 inch laminate and glass-glass and glass-polycarbonate laminates bonded with a modified polyvinylbutyral and the polyvinylbutyral presently used in safety windows.

4. PHYSICAL CHARACTERIZATION OF THE TRANSPARENT LAMINATES

Obtained in a selective manner on the laminates prepared were (1) a qualitative description of their optical performance by photographing through them; (2) a determination of adhesion through ballistic impact analysis; (3) a characterization of the adhesive and laminate stability by thermocyclic exposure; and (4) a minor amount of form stability improvement through crosslinking.

a. Qualitative Optical Description

One of the best ways to demonstrate the optical clarity and freedom from distortion available in transparencies (bonded together by the various adhesives) was to visually observe and to photograph a printed surface through them. Photographs were taken both through the specimen to a printed transparency, which was back-lighted by a diffused light, and to an opaque photographic glossy from which light was reflected. In order to show differences, portions of the uncovered printed matter were also included in the photograph.

The results of the visual examination of each of the laminates are summarized in Tables III, IV, and V and are indicative of the results in general. To demonstrate the past adhesive problem, a specimen consisting of two pieces of polycarbonate bonded by a modified polyvinyl butyral and including two pieces of soda lime glass was prepared. A description of this laminate is given in Table V and photographs of this laminate were shown earlier in Figure 1. Because of the configuration of this laminate, four surfaces of the polycarbonate were exposed to the modified polyvinylbutyral. The haze is the result of the crazing of the polycarbonate by this modified polyvinylbutyral and demonstrated one of the primary problems of the polycarbonate for use in transparencies, i.e., the lack of suitable adhesives. Figure 8 is a photograph of a laminate prepared from normal polyvinylbutyral and indicates the unacceptable high degree of crazing due to this adhesive.

To demonstrate the clarity and compatibility of the ethylene terpolymer adhesive, two laminates were made which incorporated the adhesive 35772-30 (3.5% OH). One specimen consisted of two pieces of soda lime glass bonded together, and the other two pieces of polycarbonate bonded together, both with 30 mils of the material. Transmission through these two transparencies is shown in Figure 3 in Section II. Note the very slight reduction in optical transparency and that any reduction that did occur was purely a result of the polycarbonate and not of the adhesive.



Figure 8. Unmodified Polyvinylbutyral Bonded Polycarbonate Laminate Exemplifying The Problem Of Crazeing.

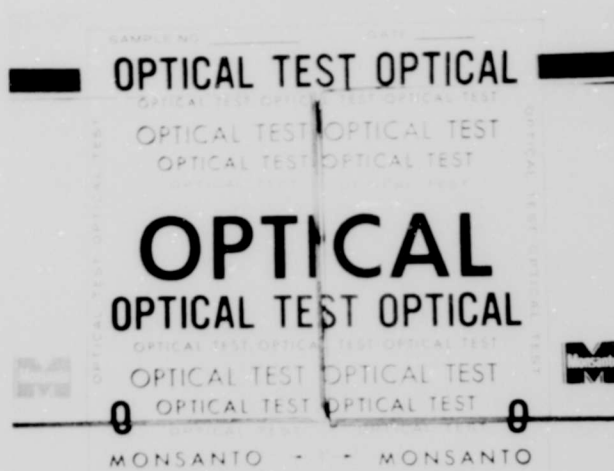


Figure 9. Glass-Polycarbonate Laminates Bonded With 10 MilS of 35772-2,0 (left) And 30 MilS Of 35772-3,0 (right).

To assist in showing the lack of any effect on transparency due to a particular ethylene terpolymer composition or to its thickness, laminates consisting of one plate of soda lime glass and one plate of polycarbonate (each 1/4 inch thick) were prepared with two different compositions at two different thicknesses. Photographs of these two laminates are shown in Figure 9. On the left is a specimen bonded together with 10 mils of the adhesive containing 1.8% OH and that on the right from 30 mils of the 3.5% OH adhesive. Note the insignificant difference in appearance between these two laminates and the small loss in the optical clarity due to either one.

Larger pieces of soda lime glass and polycarbonate (10 inch x 10 inch) of greater thickness (1/2 inch, 1/2 inch) were laminated with the ethylene terpolymer 35772-3,0 of 20 mils thickness. This is sample 696 shown in Table V. The clarity of this laminate is well demonstrated in Figure 10 at both 0° and 45° obliquity. Shown are both the clarity and freedom from distortion.

In order to demonstrate that the aluminum borosilicate glass (PPG #7428) presented no problem, 1/4 inch plates were bonded together with 20 mils of 35772-3,0. A photograph of this laminate is shown in Figure 11. Bonding of the high strength glass to polycarbonate was also demonstrated using 30 mils of the 35772-3,0; both the glass and the polycarbonate were 1 inch thick and the laminate was 6 inch x 6 inch. Photographs of this laminate at 0 to 45° are shown in Figure 4, Section II. Since the polycarbonate had been rippled slightly on the back we found it desirable also to attach a 1/4 inch thick piece of soda lime glass to eliminate any optical distortion at the surface. This laminate, therefore, was almost 1-1/2 inches thick.

The photographs of the laminates discussed above all demonstrated the excellent clarity provided by the ethylene terpolymer adhesive compound on a qualitative basis. On top of the clarity shown it was known that a certain amount of impurity existed in the ethylene due to processing and handling, since the initial material had not been made for optical purposes. It was therefore considered that the clarity could be improved to an even greater extent, and that all haze and color could be eliminated.

b. Analysis of Adhesion Through High Rate Impact

To demonstrate the adhesive quality of the ethylene terpolymer compositions, laminates were fabricated with the 35772-3,0 adhesive. One laminate consisted of two 1/4 inch pieces of soda lime glass (Table IV, 652-11); the second was a 1/4 inch piece of soda lime glass and a 1/4 inch piece of polycarbonate (Table III, 652-2); the third was aluminum borosilicate glass and polycarbonate each 1/2 inch thick (Table V, 696-3).

SAMPLE NO. 477
OPTICAL TEST OPTICAL

OPTICAL TEST OPTICAL TEST OPTICAL TEST

OPTICAL TEST OPTICAL TEST

OPTICAL TEST OPTICAL TEST

OPTICAL
OPTICAL TEST OPTICAL

OPTICAL TEST OPTICAL TEST OPTICAL TEST

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0 OPTICAL TEST OPTICAL TEST **0**

MONSANTO - - MONSANTO

0° Obliquity

SAMPLE NO. 477
OPTICAL TEST OPTICAL

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OPTICAL
OPTICAL TEST OPTICAL

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OPTICAL TEST OPTICAL TEST

0 OPTICAL TEST OPTICAL TEST **0**

MONSANTO - - MONSANTO

45° Obliquity

Figure 10. Soda Lime Glass-Polycarbonate (1/2 In. + 1/2 In.) Laminate Bonded With 35572-3,0.

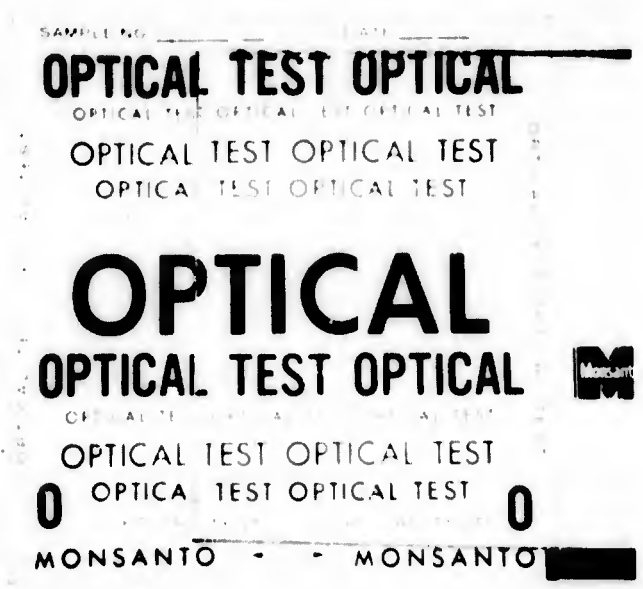


Figure 11. Aluminum Borosilicate Glass (1/4 In.) Laminate Bonded With 35772-3,0.

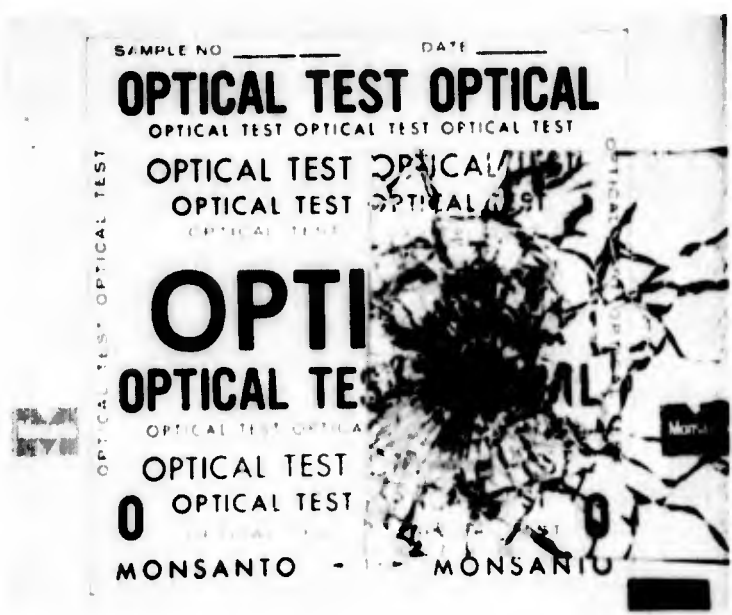


Figure 12. Soda Lime Glass-Glass Laminate Bonded With 35772-3,0 After Impact By 17 Grain Caliber 0.222 Fragment Simulator At 1000 Ft. Per Second.

To qualitatively demonstrate the adhesive ability between the 1/4 inch glass and the 1/4 inch polycarbonate and glass, the 5 inch x 5 inch laminates were impacted with a single 17-grain fragment simulator at 1000 feet per second. The results of these impacts are shown in Figure 5 and Figure 12.

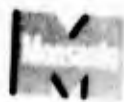
Figure 12 shows the impacted glass-glass laminate. Fracture occurred in both the front and back glass plate and considerable spalling resulted at the back plate. There was, however, no adhesive failure between the glass and the ethylene terpolymer. All failures occurred cohesively within the glass itself. The optical clarity that remained (as shown in the photograph) was evidence of the retained adhesion. (In the right portion of the figure some bubbling in the interlayer is noted. This particular imperfection was inherent in the laminate prior to impacting and had no bearing on the results).

The glass-polycarbonate laminate which was impacted on the glass side caused fracture of the glass as shown in Figure 5. As with the glass-glass laminate, the projectile, however, did not penetrate. The polycarbonate did not fracture and, as demonstrated by the retained clarity, no delamination or failure of the ethylene terpolymer adhesive resulted.

In the bottom of Figure 5 and in Figure 13 is shown the impacted high strength PPG glass-polycarbonate specimen having approximately a total thickness of 1 inch. This specimen was impacted with a caliber .30 AP projectile at about 1500 feet per second. Of prime importance in these results was the fact that no adhesive failure occurred between either the polycarbonate or the glass and the ethylene terpolymer. This is well demonstrated in the 0° obliquity photo (Figure 5) where clarity was maintained following the impact (the distortion was caused by the fractured glass). As shown in the photo in Figure 13 at 45° obliquity, viewing through such a laminate would be impossible. Any lack of performance of this laminate, however, was not due to the ethylene terpolymer and, in fact, the laminate performed as was expected.

c. Analysis of Adhesive Strength Through Thermal Cyclic Exposure

One of the best means to demonstrate the efficacy of the various adhesives for use in laminates is to prepare laminates and expose these to various thermal shock and thermal cyclic conditions. This was done and was the basis for the final screening and selection of the materials considered to be best for the application.



OPTICAL TEST OPTICAL

OPTICAL TEST OPTICAL TEST
OPTICAL TEST OPTICAL TEST



Figure 13. Aluminum Borosilicate Glass-Polycarbonate Laminate Following Impact with Caliber .30 AP Projectile At 1500 Ft. Per Second (45° Obliquity).

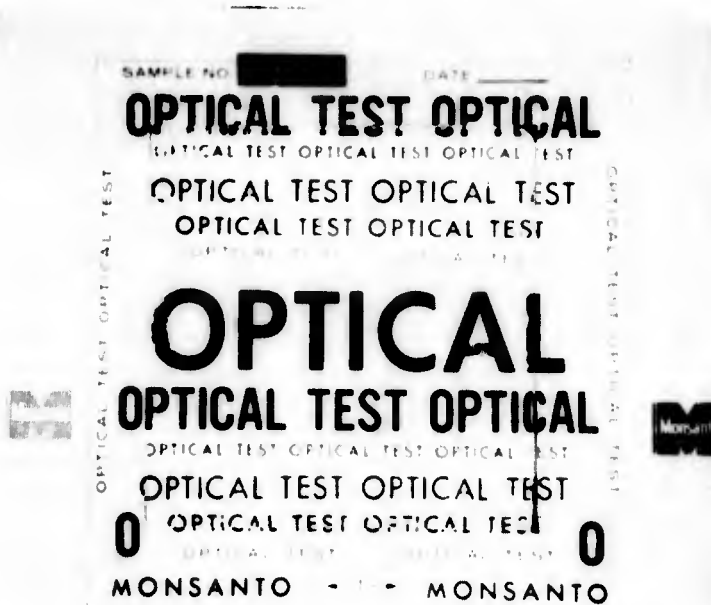


Figure 14. Soda Lime Glass-Polycarbonate Laminate Bonded With 20 Mils Of 35772-3,0 Following Thermal Shock from 180°F To -65° F.

The thermal shock exposure consisted of direct immersion of the laminate specimen into a -65°F silicone bath, followed by soaking for a period of 10 minutes, and then transferring the specimen directly into a $+130^{\circ}\text{F}$ water bath, and soaking there for an additional ten minutes. This is a quite severe test, and while it was not expected that laminates would hold up under repeated thermal shocks of this nature, the technique readily separated the better laminates from those of less interest.

The thermal cyclic exposure consisted of a cycle in which laminate was heated in an oven to 165°F (sometimes less) held for $4\text{-}3/4$ hour cooled to -65°F , and held there for $1\text{-}1/4$ hours. Both the heating and cooling of the environmental chamber occurred within 15 minutes from the start of that portion of the cycle. It was anticipated that the laminates were at temperature within 30 minutes from the start of heat-up or cool-down. This thermal cycle allowed four up-and-down excursions during a 24 hour period. However, for the most part, only one or two cycles were run per day so that visual inspection of the laminates could be conducted. Also, since cooling was provided by direct injection of liquid CO_2 the laminates were wrapped in aluminum foil to prevent non-uniform cooling of the part.

The thermal shock test was conducted on a laminate which consisted of a $1/4$ inch piece of polycarbonate and a $1/4$ inch piece of soda lime glass bonded together with adhesive 35772-3,0 (3.5% OH). This laminate is described in Table III as sample #676-1. The condition of this laminate following exposure to the thermal shock is demonstrated by the photograph in Figure 14 (in the figure some bubbles are shown around the extremities of the laminate. These bubbles were there prior to thermal exposure and were unchanged). A similar thermal shock test was conducted on a glass-glass laminate (Table V, 676-2) with similar positive results.

The above test was quite severe and consisted of a thermal shock greater than any that would be expected in an aircraft. The results, however, were indicative of the anticipated excellent performance of the ethylene terpolymer. Therefore to provide for a more realistic thermal exposure both glass-glass and glass-polycarbonate laminates containing each of the four more promising ethylene terpolymer compositions were exposed to the thermal cyclic exposure. The laminates were 5 inch x 5 inch in width and had an interlayer thickness of 20 mils:

The number of thermal cycle exposures required to fail the laminates and those particular laminates used are described in Tables III, IV, and V. For the most part, it was shown that the compositions containing 1.8, 5.3, and 7.0% OH could not withstand the thermal cycles. The compositions with the lower hydroxyl content seemed to soften at the higher temperatures, and allowed a slight amount of bubbling to occur, while those with the higher hydroxyl contents, apparently because they were too rigid, caused a shear failure in the glass (significantly, however, adhesion to the glass and the polycarbonate was maintained at these higher hydroxyl content levels).

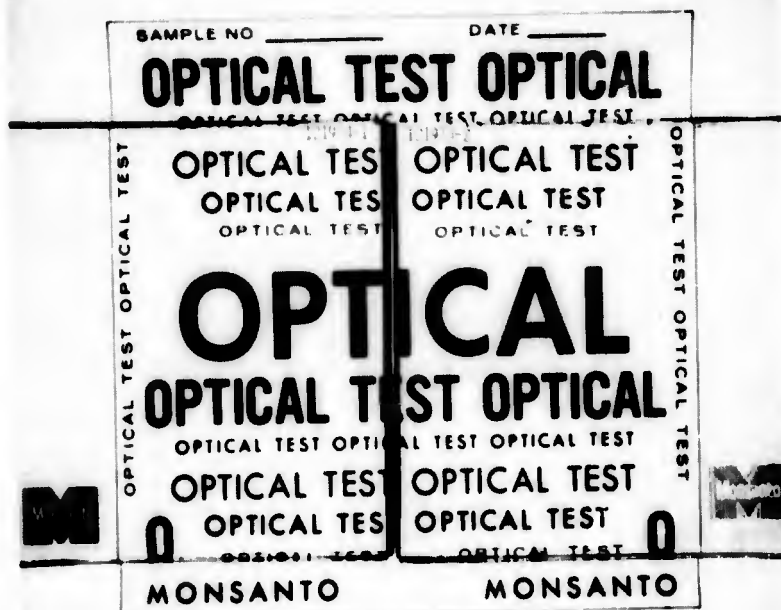
The more conclusive and interesting results were observed on the laminates bonded with 35772-3,0 (3.5% OH) and the results on glass-polycarbonate laminates are shown in Table III. There was one major difference, however, in the thermal cycles used to establish more positive results. This difference was that the thermal cycle upper temperature was limited to 130°F and raised to 140°F only after stability at the lower temperature was verified. A photograph of two of these specimens that had been thermal cycled from -65°F to +130°F for 36 cycles followed by 18 cycles from -65°F to +140°F are shown in Figure 15. Their retention of clarity indicates the retained adhesion and stability of the laminates under these conditions.

Thus, based on the thermal cyclic analysis, it was shown that the 3.5% OH ethylene terpolymer was the most promising but was limited to exposure to upper temperatures in the range of 140 to 150°F. While this limitation existed, a corrective measure was made available and will be discussed in paragraph d.

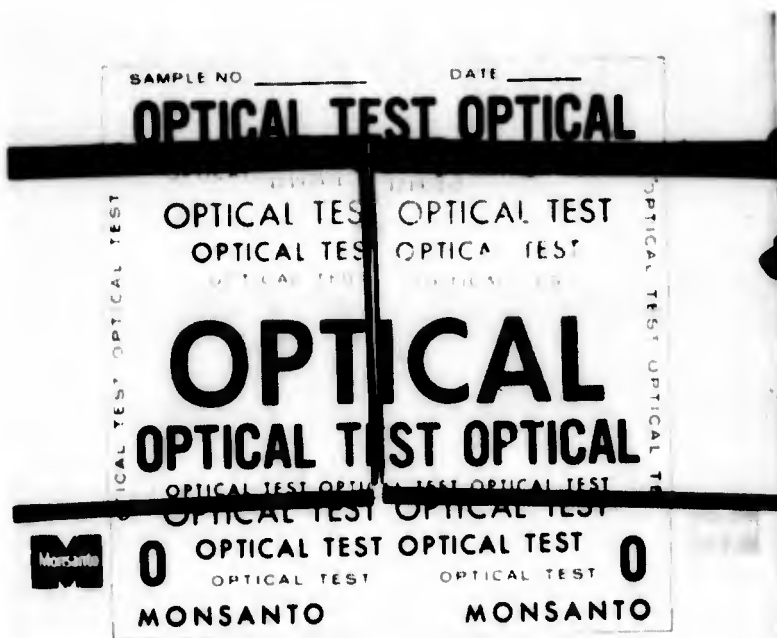
d. Incorporation of Form Stability Through Crosslinking

One of the best ways of providing form stability to a polymer at temperatures above normal softening temperatures is to incorporate a degree of crosslinking. This technique is not always usable in thermoplastic systems but in this particular instance, it is indeed applicable. These same hydroxyl groups which are part of the terpolymer and provide its adhesive strength and rigidity can be used as crosslinking sites. Naturally, their use as crosslinking sites would be competitive with their bonding characteristics.

We therefore investigated the crosslinking of the ethylene terpolymer which contained 3.5% OH. Due to the proprietary nature of the material, neither the crosslinking agent nor the technique for crosslinking can be disclosed. However, crosslinking was achieved, and it was demonstrated that the zero tensile strength (the temperature at which a material can no longer support its own weight plus a small added weight) could be increased by a factor of 40°F (from 155°F to 195°F).



0° Obliquity



(b) 45° Obliquity

Figure 15. Soda Lime Glass-Polycarbonate Laminates Bonded With 35772-3,0 Following Exposure To ca. 50 Thermal Cycles.

The zero tensile strength data for the uncrosslinked versus the crosslinked ethylene terpolymer is shown in Figure 16. Note that this represents only an indication of the form stability and does not necessarily relate to degradation temperatures.

Therefore, the feasibility of using crosslinking in this system was demonstrated and its applicability to providing additional form stability to the adhesive was indicated. Time was not available to optimize this crosslinking and to prepare laminates for inspection. Therefore, further work is required to demonstrate its actual use. Development of these techniques, however, will require only time; the development of new technology is not needed.

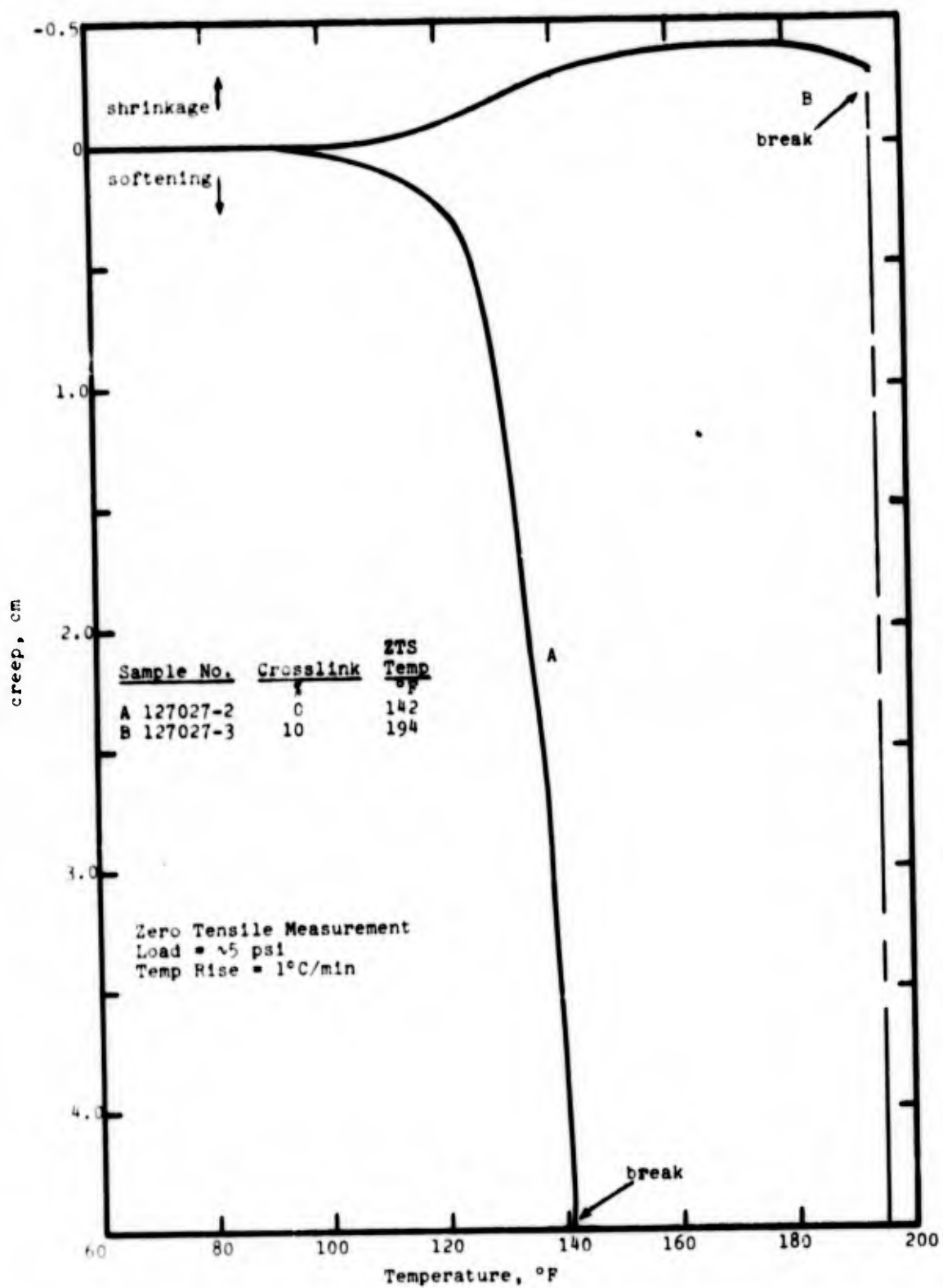


Figure 16. Zero Tensile Strength Curves for Unmodified Ethylene Terpolymer and a Crosslinked Ethylene Terpolymer.

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| 13. ABSTRACT The use of polycarbonate in transparent ballistic shields has been severely hampered by the lack of availability of suitable adhesives. In particular the thermoplastic adhesives which have had more prominence in the past are not compatible with polycarbonate. Some thermosetting materials have been available, but these too are limited due to inherent fabrication problems and sensitivity to moisture. The improved toughness of polycarbonate over acrylic, however, is sufficient to warrant the development of a suitable thermoplastic adhesive. A series of proprietary ethylene terpolymer compositions were made available by Monsanto Research Corporation. In a very limited experimental program it was shown that at least one of these compositions was found to be entirely satisfactory for bonding glass to polycarbonate. In addition to the polycarbonate compatibility, the advantages of this adhesive are that (1) it provides excellent and controllable adhesion to various glasses and polycarbonate, (2) it is elastomeric and stable over a broad temperature range, (3) it can be made crystal clear, (4) the modulus characteristics can be adjusted without the inclusion of a plasticizer, (5) the material is a thermoplastic and therefore can be handled with standard autoclaving techniques, and (6) the material potentially can be made available at a relatively low cost. It was demonstrated that glass-polycarbonate laminates bonded with the ethylene terpolymer could withstand repeated thermal cycling from -60°F to +140°F. Thus the potential for using this in unheated aircraft windshields was indicated. While not conclusively demonstrated, it was shown that the thermal cyclic stability could be increased to +165°F and probably higher. Ballistic tests at velocities up to 1500 feet per second confirm the excellent bond strength of this adhesive to both polycarbonate and glass. | | | |

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