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THE DEVELOPMENT OF

LOW TEMPERATURE CURING ADHESIVES

by

H.E. Green, J.D. Sutherland, J.M. Hom and C.H. Sheppard

TRW
SYSTEMS GROUP

ONE SPACE PARK · REDONDO BEACH · CALIFORNIA

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16. Abstract

A new approach for the development of a practical low temperature (203 K-311 K/68° F-100° F) curing adhesive system based on a family of amide/ester resins was studied and demonstrated. The work was conducted on resin optimization and adhesive compounding studies. An improved preparative method was demonstratrated which involved the reaction of an amine-alcohol precursor, in a DMF solution with acid chloride. Experimental studies indicated that an adhesive formulation containing aluminum powder provided the best performance when used in conjunction with a commercial primer.

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FOREWORD

This document constitutes the final report for the work performed by TRW Systems during the period from 28 May 1974 to 12 September 1975 under Contract NAS1-13203, "The Development of Low Temperature Curing Adhesives," sponsored by the National Aeronautics and Space Administration, Langley Research Center.

This work was conducted under the technical direction of Dr. Vernon L. Bell, Jr. of the Langley Research Center, Hampton, Virginia.

The Applied Chemistry Department of the Chemistry and Chemical Engineering Laboratory, Applied Technology Division was responsible for the work performed on this program. Dr. E. A. Burns, Manager, Applied Chemistry Department and Dr. R. J. Jones, Assistant Manager, Applied Chemistry Department, provided overall program supervision. Dr. H. E. Green was Program Manager. Major technical contributions throughout the program were provided by Mr. J. D. Sutherland, Mr. J. M. Hom and Mr. C. H. Sheppard. Acknowledgment is made of the technical assistance provided during the program by the following Applied Chemistry Department personnel.

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SUMMARY

This final report describes the work performed by TRW Systems during the period from 28 May 1974 to 12 September 1975 under Contract NAS1-13203, "The Development of Low Temperature Curing Adhesives", sponsored by the National Aeronautics and Space Administration, Langley Research Center.

The objective of this program is to provide a practical low temperature (293 K-311 K/68°F-100°F) curing adhesive system based on the new family of amide/ester resins whose feasibility was demonstrated under Contract NAS1-12309.

The current program was directed toward the optimization of the mechanical properties, synthesis, cure and stability of the most promising resin candidates. Those optimized materials were the subjects of adhesive compounding and evaluation studies. The 15-month technical program to accomplish those goals was conducted according to two principal tasks: 1) resin optimization studies and 2) adhesive compounding studies.

The major portion of the resin optimization studies was devoted to the definition of a new, more practical resin synthesis method. During that work an improved preparative method was demonstrated which involved the reaction of an amine-alcohol precursor, in a DMF solution containing an organic acid acceptor (triethylamine) with acryloyl chloride. The acrylic triester-amide of tris [hydroxymethyl] aminomethane and the acrylic diester-amide of 2-amino-2-ethyl-1, 3-propanediol (resins A-F and A-G, respectively) were prepared in greater than 90% of the theoretical yield in experiments which employed the improved synthesis as compared with the 30% to 40% typical of the interfacial reaction.

Infrared spectra of the solution prepared resins closely matched those of samples prepared by the interfacial method, and had similar cure behavior.

Attempts to prepare the amide-ester resins by an ester interchange method were largely unsuccessful. In general, resin yields from the synthetic procedures used in the simple interchange reaction were poor and there is strong evidence that amidation was incomplete in most, if not all cases. All of the resins prepared by a modified ester interchange method, involving preamidation with a cyclic anhydride followed by ester interchange, failed to cure within the acceptable temperature range.

Experimental studies were performed to determine the optimum catalyst/accelerator/stabilizer combination. The test results showed that Ionol antioxidant stabilizer at the 0.60% by weight level provided the best balance of cure rate, with methyl ethyl ketone peroxide/cobalt naphthanate (MEKP/CN) catalyst/accelerator, and resin shelf-life.

During the adhesive compounding studies a variety of adhesive and adhesive primer formulations were prepared and screened in order to select the most promising adhesive and primer combination. In addition, the properties of a recently introduced commercial, room temperature curing adhesive (B. F. Goodrich's TAME-200) was assessed.

On the basis of the studies performed, an adhesive formulation based on A-G resin and containing aluminum powder (50:50 pbw) provided the best performance when used in conjunction with TAME 200 as a primer. This combination provided lap-shear specimens with room temperature strengths in excess of 22 pascals (3250 psi). The TAME adhesive was found to gel too rapidly to be used in field repair work.

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CONTENTS (CONT'D)

I. INTRODUCTION

This final report describes the work performed by TRW Systems during the period from 28 May 1974 to 12 September 1975, under Contract NAS1-13203, "The Development of Low Temperature Curing Adhesives", sponsored by the National Aeronautics and Space Administration, Langley Research Center.

The objective of this program is to provide a practical low temperature (293 K-311 K/68°F-100°F) curing adhesive system based on the new family of amide-ester resins whose feasibility was demonstrated under Contract NAS1-12309. The amide-ester resin system was conceived to fill the urgent need for a lower temperature curing adhesive resin suitable for use in the field repair and fabrication of bonded structures. The resins were designed to aleviate the problems of excessively long cure times and/or elevated cure temperatures, and poor fatigue resistance of state of the art adhesive systems.

During the feasibility study, three candidate resins were identified as the most promising for further development on the basis of their cure behavior, moisture resistance and adhesive bond strength. The structural formulae of the three resin candidates, designated A-E, A-F and A-G, are shown below.
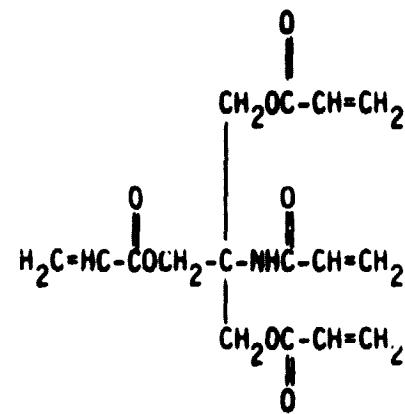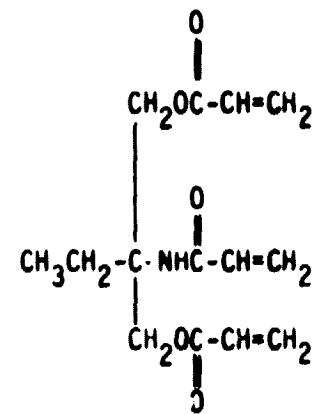
$$
\begin{array}{ccc}
\overset{\displaystyle O}{\underset{\displaystyle |}{\|}} & \overset{\displaystyle O}{\underset{\displaystyle |}{\|}} & \overset{\displaystyle O}{\underset{\displaystyle |}{\|}}\\
CH_2NHC\text{-}CH\text{=}CH_2 & CH_2OC\text{-}CH\text{=}CH_2 & CH_2OC\text{-}CH\text{=}CH_2\\
\end{array}
$$

Resin A-E   Resin A-F   Resin A-G

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The current program was directed toward the optimization of the mechanical properties, synthesis, cure and stability of the resins. Those optimized materials were then the subjects of detailed adhesive compounding and evaluation studies. The 15-month technical program to accomplish those goals was conducted according to two principal tasks. During the first task an improved, more practical resin synthesis procedure was developed and a method for the optimization of resin mechanical properties were explored. In addition, a catalyst/accelerator/stabilizer combination which afforded the best balance of cure rate and resin stability was selected.

The second principal program task was concerned with the formulation and testing of an optimized adhesive and primer combination based on the most promising resins identified during Task I.

The body of this final report is divided into two sections covering the program technical tasks: (Section II) TASK I - Resin Optimization Studies and (Section III) TASK II - Adhesive Compounding Studies. The information provided in the body of this report is supplemented by detailed accounts of experimental procedures in the Appendix.

II.   TASK I - RESIN OPTIMIZATION STUDIES

The objectives of this task were to define an improved synthesis route to the TRW amide-ester resins; to provide optimized resin mechanical properties for use from 219 K (-65°F) to 350 K (170°F) and to select the optimum catalyst/accelerator/stabilizer combination to afford the best balance of cure rate and resin stability.

Details of the Task I resin optimization studies are presented below. Representative synthetic procedures and supporting analytical data may be found in the Appendix.

2.1   RESIN PRECURSORS

All of the resin starting materials were purchased from commercial sources. The three amino-alcohols were assayed by thin layer chromatography (tlc) and neutralization equivalent titration and all were found to exceed the minimum 90% purity specification set during the previous program for use in resin synthesis.

Acryloyl chloride was purchased from several commercial sources and, on the basis of chloride analysis, was found to be of greater than 90% purity. Therefore in the initial work on this task the acid chloride was used in resin preparations without further purification. However the level of purity of some samples of the acryloyl chloride soon came under suspicion as a possible contributing cause for the nonuniform behavior of certain resin batches and subsequent samples of the acid chloride were redistilled before use.

Unless otherwise stated, all other reagents were used without further purification.

2.2   RESIN SYNTHESIS OPTIMIZATION

Although the interfacial reaction employed during the previous program (NAS1-12309) and for preparing resin samples used in the major portion of these studies is convenient for the preparation of

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small samples, it imposes a heavy cost penalty when larger quantities
(i.e., >0.5 mole) are required. This portion of Task I was devoted to
demonstrating an improved synthesis of the amide-ester resins that is
amenable to large-scale production.

The ester interchange method, frequently used in the synthesis
of esters and amides, was selected as the first synthetic method for
investigation. Ester interchange involves the reaction of an amino-
alcohol resin precursor with an excess of an acrylic ester in the
presence of an acidic or basic catalyst. An antioxidant is also present
to prevent polymerization. During the course of the reaction (shown
below for resin A-G and methyl acrylate) the alcohol produced is continu-
ously removed by distillation to drive the reaction to completion and
high yield.

$$3\ CH_2=CHCO_2CH_3 + HOCH_2\text{-}\underset{\underset{C_2H_5}{|}}{\overset{\overset{NH_2}{|}}{C}}\text{-}CH_2OH \longrightarrow CH_3CH_2\text{-}C\text{-}NHC\text{-}CH=CH_2 + 3\ CH_3OH$$
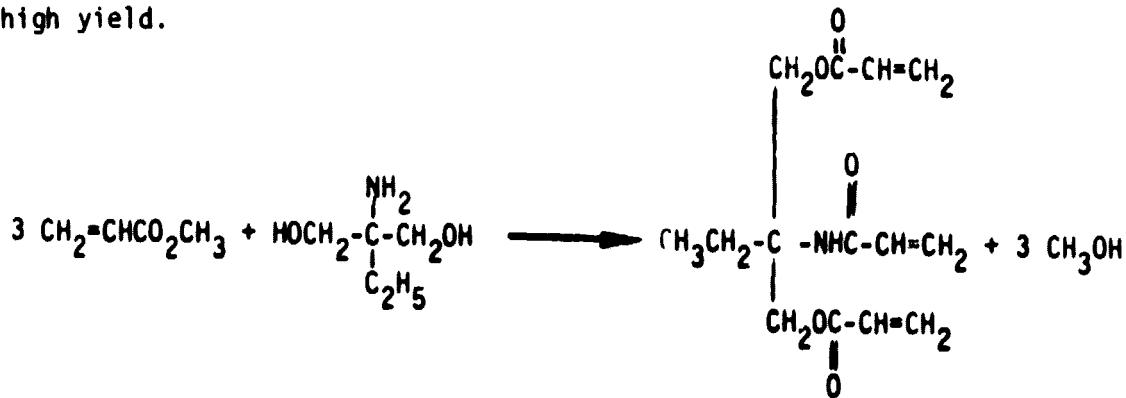
The reaction variables assessed to optimize yield and reproduci-
bility included:

● Nature of catalyst (acid or base)

● Catalyst concentration

● Acrylic ester concentration

The initial work employed methyl acrylate as the ester and 2-amino-
2-ethyl-1,3-propanediol, the amine-alcohol precursor to resin A-G, along
with several catalysts. The results of the experiments are shown in
Table I.

The experiments were performed according to a standard procedure
described in the Appendix. The most successful runs employed catalytic

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quantities of acid and/or base (No.'s 31,35 and 30). Larger than cata-
lytic quantities caused more extensive side reactions as indicated by thin
layer chromatography. When both acid and base were used the acid was
placed in the flask first and after 2 hours a sufficient quantity of base
was added to the mixture to neutralize the acid and then provide the
desired concentration. In those instances where the resin A-G was pro-
duced in the reaction, the yield was less than 10%. Thin layer chroma-
tographic (tlc) analysis of the products of the reactions performed
indicated that the yield of the desired product was reduced by competing
side reactions. There was also evidence, supplied by the infrared spectra
of the products, that the amidation reaction was competing even less
successfully than transesterification.

TABLE I

PREPARATION OF RESIN A-G

BY ESTER INTERCHANGE[a]

Run No.	Equivalent of Methyl Acrylate	Catalyst		A-G Resin Produced
		Type	Quantity (g)	
26	6.0	p-toluene Sulfonic acid	1.5	no
30	6.0	"	1.5	no
31	6.0	$NaOCH_3$	1.5	yes
32	6.0	H_2SO_4	3.0	b
34	7.4	$NaOCH_3$	16.2	yes
35	7.4	H_2SO_4/ $NaOCH_3$	1.5/ 7.06	yes
37	7.4	Aluminum isopropoxide	20.5	no
39	7.4	H_2SO_4/ $NaOCH_3$	1.5/ 3.16	yes

[a]The procedure used is described in the APPENDIX
[b]Polymerized during workup.

As a consequence of the results of the initial ester-interchange
studies described above, work on resin synthesis optimization was focused
on achieving high conversion in the amidation reaction. To simplify
the task of interpreting the results of the experiments, Jeffamine ED-600
diamine (a long-chain aliphatic ether diamine manufactured by Jefferson
Chemical Company and employed in the optimization of resin mechanical
properties subtask, Section 2.3), rather than an amine-alcohol, was used
as the resin backbone. Several catalysts and two acrylic esters, listed in
Table II, were employed in the tests. A standard procedure, described
in the Appendix was used for all of the reactions.

TABLE II

PREPARATION OF RESIN A-J6 BY ESTER INTERCHANGE

Run No.	Catalyst	Ester
63	Potassium t-butoxide	Methyl acrylate
64	Aluminum t-butoxide	Methyl acrylate
66	Perchloric acid	Methyl acrylate
67	Aluminum s-butoxide	Methyl acrylate
68	Sulfuric acid	Butyl acrylate
71	Potassium t-butoxide	Butyl acrylate

The most promising results were obtained using potassium t-butoxide
catalyst and butyl acrylate. However, even in this reaction, the yield
of diamide was judged to be less than 10%. TLC analysis of the reaction
products of all of the reactions showed a number of side products.

Since it appeared that the amide-ester resins could not be prepared
by a simple ester interchange reaction, attention was shifted toward the
evaluation of a modified interchange reaction. In earlier work performed

at TRW, it was found that when maleic anhydride is allowed to react
with an amine-alcohol, such as ethanolamine, acylation occurs almost
exclusively at the amine group. This observation suggested a route
to the amide-ester adhesive resins whereby an amine-alcohol is first
allowed to react with maleic anhydride to form an amide-acid-alcohol,
which may then be subjected to ester interchange with an acrylic ester
to give a modified amide-ester resin. The reaction sequence is illus-
trated below with amine-alcohol E and methyl acrylate.

$$HOCH_2-CH-CH_2NH_2$$
$$OH$$

$$HO-CH_2CH-CH_2NH-C-CH=CH-CO_2H$$
$$OH \quad\quad O$$

$$3\ CH_2=CHCO_2CH_3$$

$$H_2C=HC-CO_2H\ +\ 2CH_3OH\ +$$

$$CH_2NHC-CH=CH-CO_2CH_3$$
$$O$$
$$HC\!\!-\!\!-OC-CH=CH_2$$
$$O$$
$$CH_2-OC-CH=CH_2$$
$$O$$
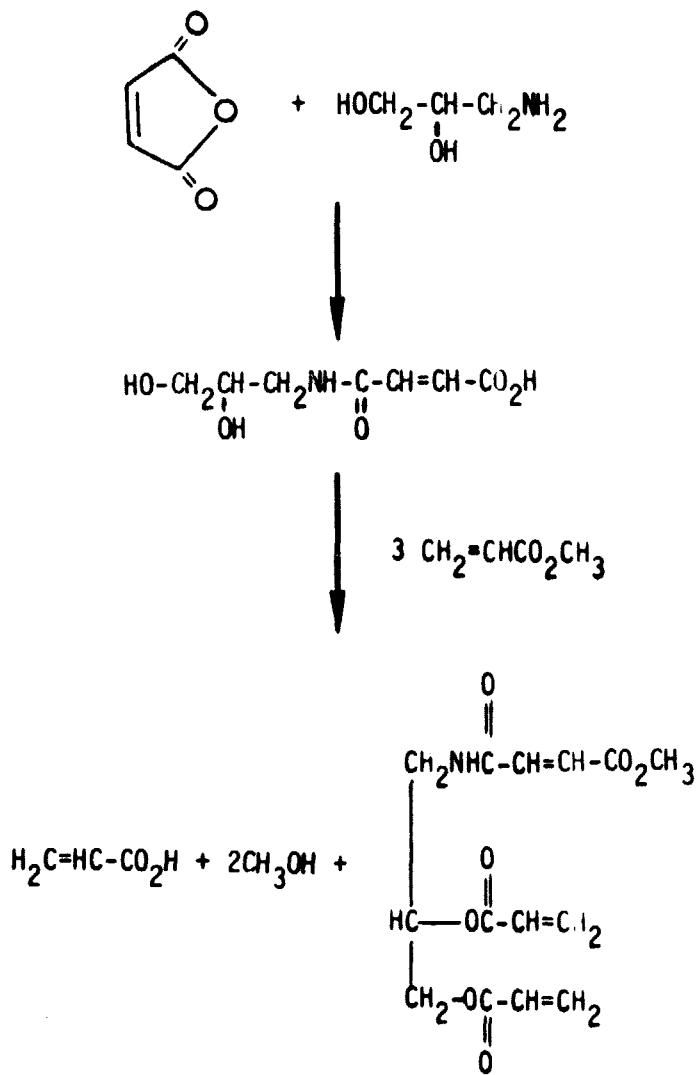
The first stage of the modified amide-ester synthesis (i.e., amidation with maleic anhydride) was successfully demonstrated using amine-alcohols E and F and with Jeffamine ED-600 diamine. The infra-red spectra of the products of the reactions showed evidence of the formation of the desired amide-acid intermediate. There was no spec-tral indication of the formation of ester during the reaction of the amine-alcohols with maleic anhydride.

The amidation step was carried out by stirring dimethyl forma-mide (DMF) or dimethyl sulfoxide (DMSO) solutions of equivalent quanti-ties of the reagents at ambient room temperature (ca. 293 K) for 16 hours. The amide-acid-alcohol products were recovered by removing the solvents on a rotary evaporator. The ester-interchange step was effected, as in the simple interchange reactions, by stirring the maleic amides with an excess of methyl acrylate at reflux. Sulfuric acid served as the catalyst for the interchange and a small quantity of Ionol antioxi-dant was added to prevent polymerization. After 4 to 6 hours at reflux, excess methyl acrylate and reaction by-products (methanol and acrylic acid) were removed by distillation.

The yields for both stages of the reaction sequence were essentially quantitative. The product of reactions beginning with the E amine-alcohol (designated AM-E) is a viscous liquid at room temperature, whereas the resin made with F (designated AM-F) is a semisolid.

Unfortunately, attempts to cure the modified amide-ester resins at room temperature with the standard MEKP/CN catalyst were unsuccessful even when ten times the usual concentration of catalyst was used. How-ever, the resins did cure within two hours at 373 K (212°F).

Several alternative solutions to the difficulties encountered in the modified ester interchange reaction sequence were investigated. One approach taken was the use of substituted, unsaturated, cyclic anhydrides to lower the melting point of the resins and increase their reactivity toward peroxide cure agents. The initial reaction run

employed dimethylmaleic anhydride (the structures of this material and
that of the other anhydrides are shown below) and F amine-alcohol.
After amidation and transesterification with methyl acrylate, a trans-
lucent, rubbery product was obtained. This material is unsuitable for
use as a room temperature curing adhesive, and no further work with
dimethylmaleic anhydride was performed.
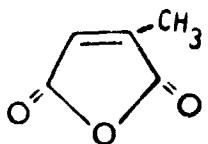
Methylmaleic Anhydride
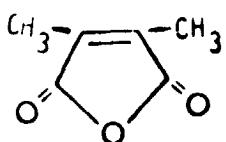
Dimethylmaleic Anhydride
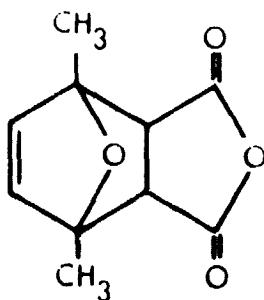
Dimethyloxinadic anhydride

Amide-acid-alcohols were also prepared from dimethyloxinadic
anhydride and methylmaleic anhydride with E and F amine-alcohols.
The amide-acid-alcohol intermediates were then subjected to trans-
esterification with methyl acrylate. All of the amide-ester resins
produced were viscous liquids and were recovered in quantitative yield.

The four resins were then employed in a series of cure experi-
ments. They were each mixed with 3% and 10% by weight benzoyl peroxide/
dimethylaniline (BP/DMA) and methyl ethyl ketone peroxide/cobalt naph-
thanate (MEKP/CN) and allowed to react for up to 48 hours at 294 K
(70° F) and at 311 K (100° F). Although none of the samples cured

completely under the test conditions, they all cured completely within
12 hours at 339 K (150°F).

Work was then discontinued on attempts to prepare amide-ester
resins by ester interchange. In general, resin yields from the synthetic
procedures used in the simple interchange reaction were poor and there is
strong evidence that amidation was incomplete in most, if not all cases.
All of the resins prepared by the modified synthesis failed to cure
within the acceptable temperature range.

A more practical resin synthesis method to replace the interfacial
method was successfully demonstrated in experiments performed subsequent
to the ester interchange work. The improved procedure involves the
reaction of an amine-alcohol, in a dimethylformamide solution contain-
ing an organic acid-acceptor (triethylamine), with acryloyl chloride.
A-F and A-G resins were prepared in greater than 90% of the theoret-
ical yield in experiments which employed the improved synthesis as
compared with the 30% to 40% typical of the interfacial reaction.
Infrared spectra of the solution prepared resins closely matched those
of samples prepared by the interfacial method. The experimental pro-
cedure for the preparation of A-G resin is in the Appendix. The pre-
paration of A-F was identical, with the exception of the change in
stoichimetry required for the quadrifunctional amine-alcohol.

Although both the solution and interfacial procedures use the
acid chloride as an acylating agent, solution reactions similar to that
employed to prepare A-F and A-G are currently used in commercial produc-
tion (e.g., to make Nomex nylon) and are, therefore, eminently practical.

2.3   OPTIMIZATION OF RESIN MECHANICAL PROPERTIES

The major effort of this portion of the Task I Resin Optimization
Studies was centered on a study of the efficacy of adding polymeric
flexibilizing agents as a method for providing optimum mechanical pro-
perties while maintaining a desirable level of environmental stability.

The flexibilizing polymers used in this study were the acrylic diamides of a series of commercially available (Jefferson Chemical Company) long-chain aliphatic ether diamines with the general structure shown below, where a, b and c may be varied to give a range of molecular weights. Initially, the acrylic diamide derived from the 600 molecular weight (MW)

$$H_2NCHCH_2-(OCHCH_2)_a-(OCH_2CH_2)_b-(OCH_2CH)_c-NH_2$$

with CH_3 groups on the indicated carbons.
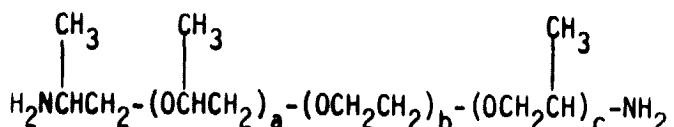
aliphatic ether diamine,designated A-J6,were employed in these studies.

Samples of A-J6 and A-F were prepared by the standard interfacial reaction procedure described in the Appendix. The AJ-6 resin was mixed with A-F resin at 10, 25 and 50% by weight diamide levels and aluminum lap-shear test specimens were prepared and tested according to the methods described in Section 3.

The results of the room temperature lap-shear strength tests are shown in Table III. In each case the major mode of bond failure was poor adhesion to the glass scrim cloth. The data do not reveal any distinct effect of the concentration of flexibilizing agent on shear strength. Since it appeared that the effect of the flexibilizing additives was likely to be masked by the variations in properties introduced by the nonuniformity of the resins prepared by the interfacial method, it was decided to discontinue work on this portion of the Task until a more reliable synthesis procedure was found.

TABLE III

LAP-SHEAR STRENGTH TESTS[a] OF A-F/A-J6 RESINS

Resin System (Weight %)	Strength[b] $N/m^2 \times 10^{-6}$ (psi)
A-F/A-J6 (90/10)	8.0 (1160)
A-F/A-J6 (75/25)	8.3 (1210)
A-F/A-J6 (50/50	7.5 (1080)

[a] Resins cured with 5% by weight MEKP/CH

[b] Quadriplicate breaks

2.4 OPTIMIZATION OF CATALYST/ACCELERATOR/STABILIZER COMBINATIONS

During Contract NAS1-12309, a hindered phenol-type antioxidant 2,6-di-t-butyl-4-methylphenol, "Ionol," was employed as a stabilizer to prevent premature gellation of the resins. Ionol was selected on a somewhat arbitrary basis because of its history of effective use in similar systems. The purpose of this portion of Task I was to test other commercially available types of stabilizers to ascertain whether they offer any advantages over Ionol.

The three stabilizers chosen for comparison with Ionol were hydroquinone, acetophenone oxime and tris(nonylphenyl)phosphite. All are representative of classes of antioxidants which work well with unsaturated resin systems and all are commercially available. The candidate stabilizers were tested by adding them to A-F resin, prepared by the interfacial method, during resin isolation at 0.05, 0.25 and 0.50 weight % levels. The resin containing the stabilizer was then cured with 5% (w/w) MEKP/CN. Satisfactory achievement of cure (crosslinking) was assessed by the insolubility/swelling characteristics of a 0.5% w,w solution of the cured material in concentrated (36N) sulfuric acid for two hours. The optimum stabilizer type and concentration was to be selected on the basis of prevention of gelation during resin isolation, inhibition of cure for more than 6, but less than 48 hours, and cost and availability.

A-F resins containing the candidate stabilizers at all three test concentrations survived the resin isolation procedure without gelling. During cure tests hydroquinone stabilized material behaved in essentially the same manner as resins stabilized by equivalent concentrations of Ionol. By contrast, the acetophenone oxime and tris(nonylphenyl)phosphite containing resins cured very rapidly and exothermically, even with reduced amounts of MEKP/CN. In some instances the samples appeared to flame briefly and emitted smoke.

The results of these tests clearly indicate that those antioxidants

do not offer any advantage over Ionol when used as stabilizers for the
TRW amide-ester adhesives.

2.5   RESIN SHELF LIFE

This portion of the Task I studies was devoted to an assessment
cf the shelf life of the amide ester resins.

Three samples of A-E resin were prepared by the standard acid
chloride synthesis route.   Each of the samples contained 0.30% by
weight of Ionol to prevent gellation during isolation.   Additional
Ionol was then added to the resins to provide test samples containing
0.37, 0.57 and 0.79 percentage by weight of the antioxidant.   After an
initial viscosity determination, the samples were monitored for changes
in viscosity at 295 K with the aid of a Brookfield disc-type viscometer.
All of the samples had gelled after 360 hours.   Gellation was rapid,
for the three samples occurring within a sixteen hour period (overnight
between 344 and 360 hours).   A similar experiment conducted with A-G
resin samples containing 0.48, 0.55 and 1.10 percentage by weight of
Ionol resulted in the gellation of all of the samples after 458 hours.

Antioxidant concentrations in excess of 1.5% by weight have been
found to inhibit cure of the amide-ester resins.   In view of the cure
inhibition which results from high Ionol concentrations and the results
of the shelf life tests described above, the antioxidant concentration
used in the adhesives formulations was maintained at the 0.6% by weight
previously used.   That concentration provides adequate protection from
premature gellation during resin isolation and at the same time allows
full cure within 48 hours with the MEKP/CN catalyst/acceleration system.

III.   TASK II - ADHESIVE COMPOUNDINC STUDIES

The primary effort durinq the initial phase of the adhesive compounding studies was to select a primer system for the adhesive studies. The generic classes of primer systems evaluated were the epoxy-amine hardener system and the modified acrylic coating system. This work included the screening, testing and compounding of the various candidate systems. After the primer selection phase, adhesive formulary work was conducted. The test results at that time strongly indicated that the amide-ester resins had relatively poor adhesion to the substrates studied and appeared to be brittle. Consequently, in order to more clearly define the actual properties of the system, the use of double lap-shear panels was adopted. At the same time a sample of the new toughened modified acrylic adhesive, TAME was obtained from B. F. Goodrich and evaluated both as a primer and adhesive.. The final system was then sleected and a series cf mechanical properties determined. Details of the fabrication of test specimens are provided below along with the analysis of testing results and conclusions derived from the data.

3.1   PRIMER SCREENING

The primary effort during the initial phase of the adhesive compounding studies was to screen potential primer resin systems prior to the final primer selection. The generic classes of primer systems evaluated were the epoxy-amine hardener system, the epoxy-polyamide amine hardener system and the modified acrylic coating system. Details of the work performed are described below.

The amide-ester resins selected for study (A-G and A-E) were prepared as previously described in a 100 percent solids state. In order to evaluate the effectiveness of the primer coating a cascading factorial test matrix was designed to study the effects of primer "B" staging versus end lap shear strength at 295 K (R.T.) and 343 K (160°F).

The initial screening of epoxy resins included combinations of three epoxy resins and three epoxy hardeners. Lap shear panels evaluated all of the primer systems at 315 K (110°F) "B" staging temperature at one and seven day time periods. Using the results obtained from these tests a second set of panels was fabricated using A-E resin and the primers selected on the basis of the 315 K (110°F) experiments. During these second tests, the primers were cured at 333 K (140°F) for one and for seven days respectively, on aluminum substrates. Lap-shear panels were fabricated using A-E resin cured for 72 hours at 295 K (72°F) and then tested at 295 K and at 343 K (160°F).

To test the effect of the addition of aluminum powder to the primer (a technique which is commonly used to minimize differences of thermal expansion between adhesive and adherends), a second set of panels was fabricated using Alcoa 101 aluminum powder as filler at the 25 and 50 parts by weight (pbw) levels.

3.2 LAP SHEAR PANEL FABRICATION

The lap shear panels were prepared by a procedure consisting of coating the cleaned (FPL chromic acid etch) faying surfaces of 2024T3 clad aluminum substrate with a primer solution and drying it in an air circulating oven for the required time (i.e., either one or seven days). At the end of the "B" staging cycle lap shear panels were fabricated utilizing the amide-ester resins (A-G and A-E) with 5% w/w MEKP/CN as the catalyst system. The lap shear panels were cured in a six place bonding fixture for 72 hours at 295 K under a pressure of approximately 0.03 to 0.07 pascals. Control valves for the resin/catalyst without primer were obtained using precisely the same processing conditions.

3.3 TEST RESULTS FOR PRIMER SCREENING

The lap-shear data for the primer system were evaluated by ranking the lap-shear values for the two amide-ester resins at the test temperatures, (see Table IV). The rankings of the various primers

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TABLE IV
SUMMARY LAP-SHEAR DATA OF INITIAL PRIMER SCREENING

Primer	Hold Temp K(°F)	Hold Time Days	Test Temp K(°F)	Lap Shear Values	
				A-G Pascals (psi)	A-E Pascals (psi)
EPOTUF 37-130 VERSAMIDE 25	315 (110)	1	295 (R.T.)	6.9 (1000)	8.5 (1240)
			343 (160)	1.4 (200)	2.0 (290)
		7	295 (R.T.)	5.1 (740)	7.7 (1120)
			343 (160)	2.7 (390)	5.3 (770)
EPON 828 EPICURE 87	315 (110)	1	295 (R.T.)	2.5 (370)	5.7 (830)
			343 (160)	3.0 (430)	3.9 (570)
		7	295 (R.T.)	4.5 (660)	7.4 (1080)
			343 (160)	4.1 (600)	6.8 (990)
EPOTUF 37-130 37-622	315 (110)	1	295 (R.T.)	5.6 (810)	4.9 (710)
			343 (160)	3.0 (440)	4.5 (650)
		7	295 (R.T.)	7.9 (1140)	7.5 (1090)
			343 (160)	5.9 (860)	9.3 (1350)
EPON 828 VERSAMIDE 25	315 (110)	1	295 (R.T.)	6.6 (950)	8.0 (1160)
			343 (160)	1.4 (200)	1.9 (270)
		7	295 (R.T.)	5.9 (860)	7.1 (1030)
			343 (160)	2.7 (390)	5.0 (720)
EPIREZ 5071 EPICURE 87	315 (110)	1	295 (R.T.)	3.7 (540)	5.2 (750)
			343 (160)	1.9 (280)	3.1 (450)
		7	295 (R.T.)	3.0 (440)	7.0 (1010)
			343 (160)	2.9 (420)	6.1 (890)
ROHM & HAAS B48N	315 (110)	1	295 (R.T.)	5.9 (860)	7.0 (1020)
			343 (160)	0.7 (100)	1.7 (250)
		7	295 (R.T.)	5.5 (800)	7.2 (1040)
			343 (160)	0.7 (100)	1.4 (200)
No Primer	-	-	295 (R.T.)	-	2.9 (425)
No Primer	-	-	295 (R.T.)	5.5 (800)	

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(Table V) were summed and those with the lowest numerical values
(i.e., Epotuf 37-130, 37-622 and Epotuf 37-130, Versamid 25) were
then selected for additional testing of the systems after "B" staging
the primer at 333 K (140°F) at one and seven days. The results of
the B staging studies at 333 K (140°F) along with the aluminum filler
study are presented in Table VI. The results of the primer study at
this time indicated the primary mode of failure of the samples was
between resin and primer and that primer cure time has relatively little
influence on shear strength. On the basis of these tests, EPOTUF 37-130
resin and 37-622 hardener filled with 50 pbw aluminum powder comprised
the most promising overall primer system.

3.4 ADHESIVE MODIFIER STUDIES

After selection of the primer system the effects of a number of
resin modifiers were evaluated according to the test matrix shown in
Tables VII and VIII. The modifier test matrix (Table VII included
copolymers (Lytron styrene-maleic and A-J9 Jeffamine-acrylic), thickener
(CAB 501-0.01 cellulosic ester and Elvalite polymethacrylate), promoters
(acrylic acid) and peroxide levels. In addition to the lap shear speci-
mens comprising the test matrix, two panels were fabricated using only
the A-E resin at two peroxide levels. A third control panel was fabri-
cated using only the primer system. The test matrix shown in Table VIII
included epoxy maleic adducts, two levels of copolymer and two levels
of catalyst/accelerator. Processing was identical to panels in the
primed and adhesive/modifier studies.

The results of these studies (see Tables IX and X) did not show
any improvement in lap-shear strength using these modifications. Fail-
ure mode in all cases was adhesion to the primer. Therefore, because
adhesive resin brittleness is a known factor causing adhesive failures
(the other major factor being lack of adhesion caused by poor surface
wetting and/or surface reactivity), it was decided to determine the
lap-shear strength values using double lap shear test specimens.

TABLE V

PRIMER SYSTEM RATING

PRIMER	1 Day 315 K (110°F)				7 Day 315 K (110°F)				
	A-G		A-E		A-G		A-E		TOTAL
EPOTUF 37-130 37-622	4[1]	1[2]	6[1]	1[2]	1[1]	1[2]	2[1]	1[2]	17
EPON 828 VERSAMIDE 25	2	4	2	5	4	4	4	5	30
EPOTUF 37-130 VERSAMIDE 25	1	4	1	4	2	4	1	4	21
EPON 828 EPICURE 87	6	2	4	2	5	2	3	2	26
EPIREZ 5071 EPICURE 87	5	3	5	3	6	3	6	3	34
ROHM & HAAS B48N	3	5	3	6	3	5	5	6	36

[1] Rating indicates order of system when ranked by 295 K (R.T.) lap shear values

[2] Rating indicates order of system when ranked by 343 K (160°F) lap shear values

TABLE VI

SUMMARY OF LAP-SHEAR DATA OF PRIMER STUDY

Primer	Hold Temp K (°F)	Hold Time Days	Test Temp K (°F)	Lap Shear Values[a] A-E Pascals (psi)	Failure Mode
EPOTUF 37-130 37-622	333 (140)	1	295 (R.T.)	4.3 (630)	Resin Primer
			343 (16)	4.5 (660)	Resin Primer
		7	295 (R.T.)	4.3 (630)	Resin Primer
			343 (16)	3.0 (440)	Resin Primer
EPOTUF 37-130 VERSAMIDE 25	333 (140)	1	295 (R.T.)	6.1 (890)	Resin Primer
			343 (16)	3.4 (490)	Resin Primer
			295 (R.T.)	6.5 (940)	Resin Primer
			343 (16)	4.7 (630)	Resin Primer
EPOTUF 37-130 37-622 (25 pbw Al Powder)	315 (110)	7	245 (R.T.)	8.8 (1280)	60 Cohesive
			343 (16)	8.5 (1230)	70 Cohesive
			295 (R.T.)	8.5 (1240)	80 Cohesive
			343 (16)	5.4 (790)	50 Cohesive
EPOTUF 37-130 VERSAMID 25 (25 pbw Al Powder)	315 (110)	7	295 (R.T.)	7.4 (1080)	Resin Primer
			343 (16)	4.5 (650)	Resin Primer
			295 (R.T.)	7.4 (1070)	Resin Primer
			343 (16)	4.3 (630)	Resin Primer
EPOTUF 37-130 37-622 (50 pbw Al Powder)	315 (110)	7	295 (R.T.)	11.1 (1610)	80 Cohesive
			343 (16)	9.0 (1310)	95 Cohesive
			295 (R.T.)	6.5 (950)	Resin Primer
			343 (16)	5.3 (770)	Resin Primer
EPOTUF 37-130 VERSAMID (50 pbw Al Powder)	315 (110)	7	295 (R.T.)	6.2 (900)	60 Cohesive
			343 (16)	2.6 (380)	Resin Primer
			295 (R.T.)	8.4 (1220)	Resin Primer
			343 (16)	3.6 (520)	Resin Primer

a) The 295 K lap-shear strength of the resin without primer is 2.9 pascals (425 psi)

TABLE VII

ADHESIVE/MODIFIER MATRIX STUDY

Experiment	Modifications[a]			
	A	B	C	D
1	-	-	-	-
2	+	-	-	+
3	-	+	-	+
4	+	+	-	-
5	-	-	+	+
6	+	-	+	-
7	-	+	+	-
8	+	+	+	+

a) Modifications:

		+	-
A -	Copolymer Adhesives	Lystron 810	Jeffamine Acrylic A-J9
B -	Chemical Thickener	Cellulosic Ester CAB 501-.01	DuPont Elvalite Polymethacrylate
C -	Adhesive Promoter	With Acrylic Acid	Without Acrylic Acid
D -	Peroxide Level	High (10 Drops MEKP/ 5 Drops CN/ Gram of Resin)	Low (5 Drops MEKP/5 Drops CN/Gram of Resin)

TABLE VIII

EPOXY-MALEIC ADDUCT EVALUATION MATRIX

Catalyst/Accelerator Level[1]	Level of AE/Epoxy Maleic Adduct	
	75/25	50/50
High	$x^{(2)}$	$x^{(2)}$
Low		$x^{(2)}$

(1) See Table VII for quantity of catalyst/accelerator

(2) One set contained EPOTUF 37-130 - Maleic Adduct
   One set contained EPON 828 - Maleic Adduct

The single lap-shear test specimen design introduces significant peel stress into bonded joints during loading. Relatively brittle adhesives are usually tested on double lap-shear specimens because this specimen configuration minimizes peel stress during the test (Reference 1). Two sets of double lap-shear specimens (see Figure 1) were fabricated using A-E and A-G resin systems. The double lap-shear test values are reported in Table XI along with comparative values of the single lap-shear test specimen. As can be seen, the values were somewhat better than the lap-shear values of the single lap-shear test specimen but still below the desired strength levels.

3.5 EVALUATION OF TAME 200 ADHESIVE

B. F. Goodrich has introduced to the commercial market a family of new adhesives which claim several performance advantages over most two part room temperature curing adhesives. This line of toughened acrylic adhesives is now being marketed under the trade name "TAME".

The proposed application area (i.e., field repair of aircraft components) for the low temperature curing adhesive requires unique performance and/or processing characteristics. The characteristics required include: a room temperature curing system to prevent stress accumulation; adequate working life for the adhesive; the ability to bond a variety of materials with minimum surface preparation, reasonable resistance to chemical degradation and mechanical properties sufficient for structural applications.

For comparative purposes a series of screening tests were conducted using the TAME adhesive. The panels were fabricated with 2024T3 aluminum alloy and TAME 200 adhesive catalyzed with 3% w/w Goodrich Catalyst C. The lap-shear panels were assembled on a six place bonding fixture, cured 24 hours at 298 K (R. T.), machined and then tested. Control lap-shear values for the TAME adhesive include tests at 298 K (R. T.), 218 K (-67°F) and 343 K (160°F) (Table XII). The remaining test specimens were

TABLE IX

SUMMARY LAP SHEAR DATA OF ADHESIVE/MODIFIER STUDY

Panel #	Test Temp K (°F)	Lap Shear Values		
		Pascal	(psi)	Failure Mode
1	295 (R.T.)	4.5	(650)	Resin Primer
	343 (160)	4.2	(610)	Resin Primer
2	295 (R.T.)	4.9	(710)	Resin Primer
	343 (160)	8.6	(1270)	Resin Primer
3	295 (R.T.)	4.8	(690)	Resin Primer
	343 (160)	4.5	(660)	Resin Primer
4	295 (R.T.)	2.8	(400)	Resin Primer
	343 (160)	3.7	(530)	Resin Primer
5	295 (R.T.)	5.2	(760)	Resin Primer
	343 (160)	5.9	(860)	Resin Primer
6	295 (R.T.)	4.5	(660)	Resin Primer
	343 (160)	7.5	(1090)	Resin Primer
7	295 (R.T.)	5.6	(810)	Resin Primer
	343 (160)	4.1	(600)	Resin Primer
8	295 (R.T.)	2.5	(370)	Resin Primer
	343 (160)	6.1	(890)	Resin Primer
Control[1]	295 (R.T.)	8.4	(1220)	Resin Primer
	343 (160)	10.3	(1490)	Resin Primer
Control[2]	295 (R.T.)	6.9	(1000)	Resin Primer
	343 (160)	10.3	(1490)	Resin Primer
Primer Only	295 (R.T.)	17.2	(2500)	Cohesive
	343 (160)	10.8	(1570)	Cohesive

(1) High catalyst level (see Table VII)

(2) Low catalyst level (see Table VII)

TABLE X

SUMMARY LAP-SHEAR DATA EPOXY-MALEIC ADDUCT

Epoxy Maleic Adduct	Adduct Level	Test Temp K (°F)	Lap-Shear Values		
			Pascals	(psi)	Failure Mode
EPOTUF 37-130/ Maleic	50/50	295 (R.T.)	3.5	(510)	Resin Primer
		343 (160)	3.0	(420)	Resin Primer
	75/25	295 (R.T.)	1.4	(210)	Resin Primer
		343 (160)	2.2	(320)	Resin Primer
(1)	50/50	295 (R.T.)	4.3	(620)	Resin Primer
		343 (160)	2.6	(380)	Resin Primer
EPON 828/ Maleic	50/50	295 (R.T.)	4.3	(630)	Resin Primer
		343 (160)	2.8	(400)	Resin Primer
	75/25	295 (R.T.)	-	delam	Resin Primer
		343 (160)	3.3	(480)	Resin Primer
(1)	50/50	295 (R.T.)	5.2	(750)	Resin Primer
		343 (160)	3.2	(460)	Resin Primer

(1) Quantity of peroxide catalyst MEKP double with the quantity of CN remaining the same.

TABLE XI

Comparison of Single and Double Lap-Shear Properties

Resin Matrix	Test Temperature K (°F)	Lap-Shear Values Pascals (PSI)	Failure Mode
A-E (1)	298 (R.T.)	2.9 (420)	Adhesive
(2)	298 (R.T.)	5.5 (800)	Adhesive
A-G (1)	298 (R.T.)	5.8 (840)	Adhesive
(2)	298 (R.T.)	7.9 (1140)	Adhesive

(1) Single Lap-Shear Test   MM-A-132
(2) Double Lap-Shear Test   (Reference 1)
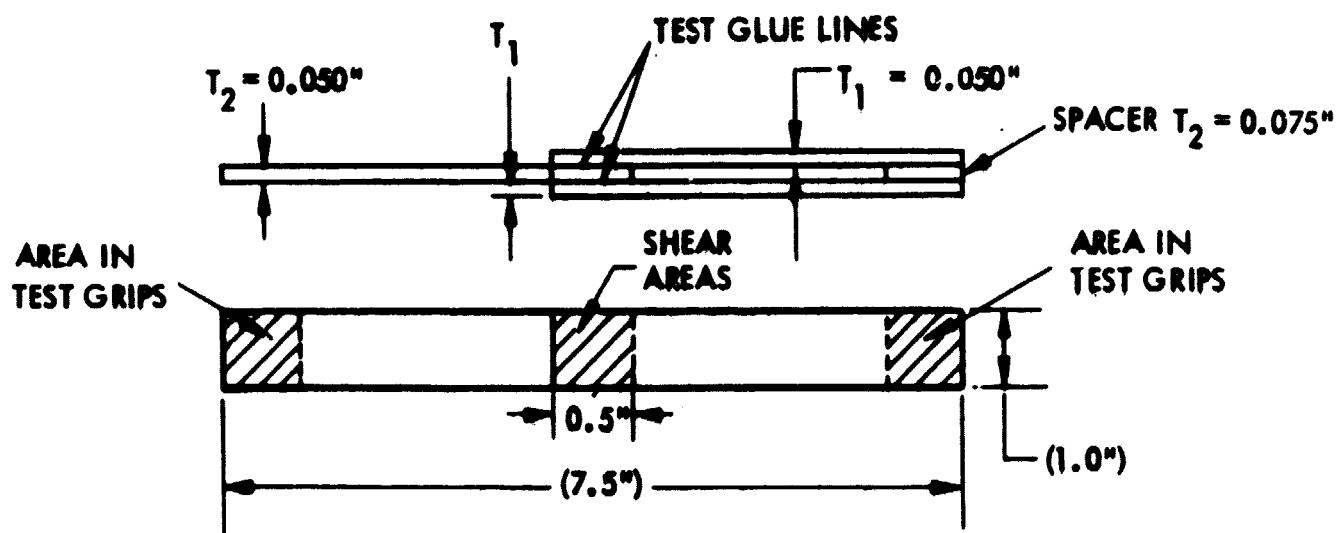

Figure 1.   Double Lap-Shear Specimen

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then subjected to the following environments, those data are also presented in Table XII.

- 2 Hour Water Boil
- 7 Days MEK Immersion
- 30 Days 322 K (120°F), Condensing Humidity
- Isothermal Aging at 343 K (160°F) for 300,
  500 and 1000 hours.

The results of these tests (Table XII) show reasonable correlation with the B. F. Goodrich data sheet for TAME 200 and demonstrated the good adhesion of TAME 200 for bonding other substrates i.e., titanium and graphite/epoxy composites using short beam shear specimens. Results from this study (see Table XIII) confirmed the excellent adhesion of TAME 200 to those substrates. Peel strength test panels then

were fabricated from thin aluminum alloy sheet. Considerable difficulty was encountered in fabricating an acceptable panel because the TAME 200 gels very rapidly and also forms a skin almost immediately after coating the adherend surface. Good adhesion between adherends is not achieved after gelling or skinning of the TAME 200. This problem has been reported during conversations with other users of TAME 200 adhesive and apparently is characteristic of the material. Consequently, TAME 200 cannot be considered as a viable adhesive candidate for field repair of adhesive joints. However, because TAME 200 adheres very well to substrates it was selected as an adhesive primer for evaluation with the amide-ester adhesive resins.

3.6   ADHESIVE SCREENING WITH TAME 200 PRIMER

The primers evaluated during this study consisted of TAME 200, TAME 200/amide-ester resin blends and an epoxy primer. Adhesives evaluated consisted of the A-G and A-E amide-ester resins with and without aluminum powder as a reinforcing filler. The results of this study (see Table XIV) indicate that the TAME 200 primer/A-G resin with

TABLE XII

LAP-SHEAR TESTING OF TAME 200 ADHESIVE

Test Condition	Test Temperature K (°F)	Aging Time Hours	Aging Temp K (°F)	Lap-Shear Strength	
				Pascals (PSI)	Failure Mode
Control	298 (R.T.)	0	-	28.1 (4080)	Cohesive
Control	218 (-65)	0	218 (65)	20.9 (3030)	Cohesive
Control	343 (160)	0	343 (160)	24.3 (3520)	Cohesive
Isothermal Aging	298 (R.T.)	300	343 (160)	29.2 (4230)	Cohesive
	298 (R.T.)	500	343 (160)	26.4 (3830)	Cohesive
	298 (R.T.)	1000	343 (160)	25.8 (3740)	Cohesive
MEK Immersion	298 (R.T.)	168	298 (R.T.)	Delaminated	
2 Hours Boiling H_2O	298 (R.T.)	2	372 (212)	30.1 (4370)	Cohesive
Humidity	298 (R.T.)	720	321 (120)	32.4 (4700)	Cohesive
Stressed Aging	298 (R.T.)	1000	343 (160)	15.8 (2270)[1] 18.2 (2620)[2]	Cohesive Cohesive

1 - Specimens loaded @ 20% ultimate stress @ (160° F)

2 - Specimens loaded @ 40% ultimate stress @ (160° F)

NOTE: The specimens loaded @ 60% and 80% ultimate stress @ 160° F failed before end of 1000 cycle.

TABLE XIII

SUMMARY OF T-PEEL AND SHORT BEAM SHEAR)ATA OF TAME 200 ADHESIVE

Test Temperature K (°F)	Substrates	Short Beam Shear Stress Pascals (PSI)	T-Peel N/CM (LBS/IN)
298 (R.T.)	2024T3 Aluminum/ 2024T3 Aluminum	71.8 (10,400)[1]	-
343 (160)		47.5 (6,890)	-
298 (R.T.)	6A14V-Titanium/	63.3 (9,180)[2]	-
343 (160)	2024T3-Aluminum	55.2 (8,010)	-
298 (R.T.)	Epoxy Graphite/	42.2 (6,120)[3]	-
343 (160)	2024T3 Aluminum	35.6 (5,160)	-
298 (R.T.)	2024T3 Aluminum/ 2024T3 Aluminum	-	11.4 (6.5)[4]

(1) Failure occurred after aluminum substrate exhibited bending under loading bar. Specimen length 6T with testing span being 4T.

(2) Failure occurred with aluminum being bent. Specimen tested with Titanium substrate next to reaction bar (see Note 1 for specimen size).

(3) Failure occurred within Graphite Epoxy Composite (see Note 1 for specimen size).

(4) Average of 8 specimens. Range for test specimens 9.8 - 14.0 N/cm (5.6 - 8 lbs/in).

TABLE XIV

SUMMARY OF DOUBLE LAP-SHEAR TEST SPECIMEN RESULTS

Test Temperature	Primer	Acrylic Amide Ester Type	Lap-Shear Strength	
			Pascals (PSI)	Failure Mode
298 (R.T.)	None	A-G	6.5 (950)	Adhesive
343 (160)		A-G	5.7 (820)	Adhesive
298 (R.T.)	Epoxy	A-G	4.5 (660)	Adhesive to
343 (160)			5.2 (750)	Primer
298 (R.T.)	TAME 200[1]	A-G	20.5 (2980)	Adhesive to
343 (160)			5.1 (740)	Primer
218 (-65)			11.6 (1680)	
298 (R.T.)	TAME 200[1]	A-G (Al filled at 50:50 PBW)	24.4 (3540)	Adhesive to
343 (160)			7.1 (1020)	Primer
298 (R.T.)	Epoxy	A-E	7.6 (1110)	Adhesive to
343 (160)	(EPI-CURE R15)		7.9 (1140)	Primer
298 (R.T.)	TAME 200[1]	A-E	11.8 (1710)	Adhesive to
343 (160)			9.6 (1390)	Primer
218 (-65)			5.5 (800)	
298 (R.T.)	TAME 200/A-G	A-G (Al filled at 50:50 PBW)	10.5 (1520)	Adhesive primer
343 (160)	(90:10 PBW)		12.1 (1750)	to Aluminum
298 (R.T.)	TAME 200/A-G	A-G (Al filled at 50:50 PBW)	8.4 (1220)	Adhesive Primer
343 (160)	(70:30 PBW)		9.2 (1330)	to Aluminum

(1) Open time for primer was 30 minutes (tack free) at 298 K (R.T.)

aluminum powder (50:50 PBW) adhesive system provided the highest values at 298 K (77° F). However, a blend of TAME 200 and A-G amide-ester resin (90:10 PBW) as the primer provided higher values at 343 K (160°F). This may be attributed to additional cure of the system at 343 K (160°F). Because satisfactory values (i.e., >20 Pascals) were not obtained with the A-E amide-ester resin it was decided to discontinue its evaluation.

3.7 DETAILED CHARACTERIZATION STUDIES

The detailed characterization studies were designed to obtain preliminary adhesive properties of the A-G amide-ester acrylic resin system and the TAME 200 primer. The mechanical property data obtained during this series of tests included the lap-shear ultimate strength, short beam shear strength, T-peel and residual stress. Details of the panel fabrication, testing and testing results are presented below.

3.7.1 FABRICATION PROCEDURE FOR DOUBLE LAP-SHEAR SPECIMENS

The 2024T3 aluminum alloy faying surfaces were solvent cleaned (vapor degreased), then immersed in 339 K (150°F) chromic acid for 15 minutes, washed with cold tap water, rinsed with cold distilled water and oven dried in a 339 K (150°F) air circulating oven. Immediately after drying, the panels were coated with TAME 200 adhesive (primer) and allowed to cure 30 minutes at ambient conditions. The panels were then coated with the amide-ester adhesive (50 pbw A-G resin: 50 pbw aluminum powder) assembled and allowed to cure 72 hours at ambient conditions prior to testing.

On the series of double lap-shear specimens using the substrate combination of aluminum alloy/epoxy graphite, a slightly different specimen configuration, commonly employed with dissimilar adherends, was utilized (Figure 2). In the Figure 2 the long strips are aluminum, the short ones are the epoxy-graphite.
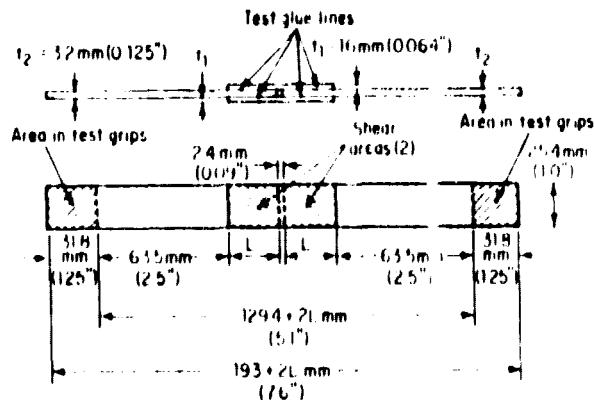
Figure 2.   Dissimilar Adherend Double Lap Shear Specimen

The aluminum faying surfaces were prepared as described above, with the epoxy graphite composite being prepared by solvent washing with acetone. The primer application and cure and adhesive application and cure were identical to the aluminum double lap-shear specimens.

3.7.2   SHORT BEAM SHEAR SPECIMENS

In fabricating the short beam shear specimens 2024T3 aluminum strips 3.18 mm (.125-in) x 6.35 mm (.250-in) x 203.5 mm (8-in) were chemically cleaned using the FPL chromic acid etch. In the case of the aluminum/epoxy graphite specimens, the graphite composite was solvent cleaned with acetone. The TAME 200 adhesive primer was then coated onto the cleaned faying surfaces, cured for 30 minutes at ambient conditions, the amide-ester adhesive coated and then the specimens cured in a bonding fixture for 72 hours.

3.7.3   RESIDUAL STRESS SPECIMENS

The specimen configuration used in the fabrication of the residual stress specimens included 2024T3 aluminum alloy, 6A14V titanium alloy, 17-7 pH stainless steel and epoxy graphite composite. The cleaning methods used to prepare the faying surfaces were as follows:

Aluminum Alloy - FPL Chromic Acid Etch

6Al4V Titanium Alloy - TURCO 5578 Alkaline Etch

17-7 PH Stainless Steel - Hot chromic acid etch (concen-
trated chromic acid)

Epoxy Graphite Composite - Solvent wash with acetone

The TAME adhesive primer and the amide-ester adhesive were applied
and cured as previously described for the short beam shear specimens.

3.7.4   T-PEEL SPECIMENS

The panels from which the T-peel specimens were machined were
fabricated using 0.25 mm (.010-in) x 228.6 mm (9-in) x 228.6 mm (9-in)
2024T3 aluminum alloy. The cleaning, priming and curing were as pre-
viously described for test specimens using the aluminum alloy.

3.8   TESTING AND RESULTS

After curing the amide-ester adhesive, the panels were machined
and the specimens tested. The results of the double lap-shear specimen
tests are presented in Table XV, the short beam shear specimen results
in Table XVI, and the residual stress specimens results in Table XVII.

The results of these characterization tests are, in general dis-
appointing. Although the room temperature lap-shear strength is in an
acceptable range (22.4 pascals), failure at the primer-resin interface
indicates that the resin system is still deficient in adhesion. In
addition, the results of the T-peel rests at room temperature (1.75 N/cm;
1 lb/in.) confirm previous results which indicated that the current
amide-ester system is relatively brittle.

TABLE XV

SUMMARY OF DISSIMILAR ADHEREND DOUBLE

LAP-SHEAR TESTS

Test Temperature K ('F)	Substrates	Lap Shear Strength Pascals (PSI)		Failure Mode
219 (-67)	Al/Al	12.8	(1860)	adhesive, Primer to Resin
298 (RT)		22.4	(3250)	" " " "
344 (160)		7.2	(1050)	" " " "
219 (-67)	Al/Epoxy Graphite	1.9	(270)	adhesive, Primer to Graphite
298 (RT)		7.0	(1020)	" " " "
344 (160)		5.9	(860)	" " " "

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TABLE XVI

SUMMARY OF SHORT BEAM SHEAR SPECIMENS

Test Temperature K (°F)	Specimen Substrates	Short Beam Shear Strength		
		Pascals	(PSI)	Failure Mode
219 (-67)	Al/Al	41.4	(6010)	Adhesive, Primer to amide-ester
298 (RT)		48.1	(6980)	" " "
344 (160)		28.7	(4160)	" " "
219 (-67)	Al/Epoxy Graphite	26.1	(3780)	Adhesive, Primer to Graphite
298 (RT)		24.9	(3620)	Some failed
344 (160)		26.7	(3900)	In Graphite Composite

TABLE XVII

SUMMARY OF RESIDUAL STRESS SPECIMENS

Specimen Substrates	Test Temperature K (°F)		Deflection mm (in)	
Al/Ti	293	(68)	0.00	(0.00)
	339	(150)	5.84	(0.23)
	366	(200)	5.08	(0.20)
	311	(100)	1.78	(0.07)
	293	(68)	-5.59	(-0.22)
Second Cycle				
	293	(68)	-5.59	(-0.22)
	330	(135)	-1.52	(-0.06)
	339	(150)	1.78	(0.07)
	352	(175)	3.56	(0.14)
	366	(200)	4.57	(0.18)
	339	(150)	2.79	(0.11)
	293	(68)	-5.59	(-0.22)
Al/17-7 PH Stainless Steel	293	(68)	0.00	(0.00)
	339	(150)	3.05	(0.12)
	366	(200)	3.30	(0.13)
	330	(135)	1.52	(0.06)
	293	(68)	-1.02	(-0.04)
Second Cycle				
	293	(68)	-1.02	(-0.04)
	330	(135)	1.02	(0.04)
	339	(150)	1.52	(0.06)
	352	(175)	4.32	(0.17)

SUMMARY OF RESIDUAL STRESS SPECIMENS (CON'T)

Specimen Substrates	Test Temperature K (°F)		Deflection mm (in)	
	366	(200)	4.83	(0.19)
	339	(150)	2.79	(0.11)
	293	(68)	-1.02	(-0.04)
Al/Epoxy Graphite	293	(68)	0.00	(0.00)
	339	(150)	6.35	(0.25)
	366	(200)	3.56	(0.14)
	311	(100)	-0.51	(-0.02)
	293	(68)	-9.40	(-0.37)
	293	(68)	-9.40	(-0.37)
	330	(135)	-3.56	(-0.14)
	339	(150)	-1.52	(-0.06)
	352	(175)	2.03	(0.08)
	366	(200)	3.05	(0.12)
	339	(150)	0.76	(0.03)
	293	(68)	-9.40	(-0.37)

Note: All specimens began with the aluminum down, but due to specimen curvature all specimens had to be reversed. Therefore all negative deflection measurements are with the aluminum up and all positive measurements are with the aluminum down.

IV.   CONCLUSIONS AND RECOMMENDATIONS

Summarized below are the conclusions reached during this development program and recommendations for further work based on those findings.

4.1   CONCLUSIONS

1.   An improved synthesis for the TRW amide-ester resins was developed using a solution technique. The improved procedure provided the resins in high ($\geq$90%) yield and is compatible with volume production methods.

2.   Improvements in adhesion to metals and resin toughness will have to be achieved before a practical, ready to use adhesive system based on the amide-ester resins can be provided.

4.2   RECOMMENDATIONS

1.   A detailed analysis of the parameters of the new solution method for the preparation of the resins is needed to assure the production of uniform resin batches.

2.   Work on the modification of the basic resin backbone to provide greater toughness and adhesion should be initiated to provide greater toughness and adhesion.

3.   The modified resin system should be the subject of additional adhesive compounding work to provide the desired adhesive system.

APPENDIX

Representative examples of the synthetic procedures used in this study are presented below, along with reproductions of the infrared spectra of the resins produced. The procedures employed in the preparation and testing of mechanical test specimens are described in Section 3.

1. STANDARD INTERFACIAL PREPARATIVE PROCEDURE

The following experimental procedure for the synthesis of resin A-G is representative of the interfacial method employed for the preparation of most of the resins used in this study.

A cold (ca. 273 K) solution of 27.2 g (0.3 mol) of acryloyl chloride (A) in 60 ml of dry THF was poured all at once into a one-liter blender jar containing a vigorously agitated, cold (ca. 273 K) solution of 11.9 g (0.1 mol) of 2 amino-2-ethvl-1,3-propanediol (G) and 12.0 g (0.3 mol) of sodium hydroxide. During the reaction the blender jar was cooled with an ice-water jacket to maintain a reaction temperature ≤ 293 K (68°F). Mixing was continued for 10 minutes, then the solution was extracted twice with 300-ml portions of chloroform. The combined chloroform solutions were washed twice with saturated sodium bicarbonate solution and then dried over magnesium sulfate. Ionol antioxidant (0.17 g) was added to the solution and then the cholorform was removed at room temperature under reduced pressure. The isolated resin was stored under nitrogen in a refrigerator at ca. 273 K (32°F).

A typical infrared (neat resin smear) spectrum of this resin is presented in Figure 3.

2. PROCEDURE USED FOR ESTER INTERCHANGE REACTIONS

The following procedure for the preparation of A-G resin is representative of those used in the ester interchange reactions with minor modifications dictated by the chemical and physical properties of the reagents used in specific instances.

> To a 100-ml resin kettle equipped with a mechanical stirrer, distillation apparatus, thermometer and a one-atmosphere pressure nit ogen source, were added 11.92 g (0.1 mol) 2-amino-2-ethyl-1,3-propanediol, 0.17 g Ionol antioxidant, catalyst and methyl acrylate. Stirring was begun and the contents of the vessel was heated by means of an oil bath maintained at 393 K (120°C). The mixture was allowed to relux for 2 hours, after which a distillate was collected over a 2-hour period. The remaining methyl acrylate was removed by evaporation under vacuum in an unheated oven. The residue was extracted with $CHCl_3$, washed with aqueous $NaHCO_3$, dried over $MgSO_4$ and then stripped of $CHCl_3$ under vacuum.

> An infrared spectrum of a resin produced by this procedure is shown in Figure 4.

3. PREPARATION OF A-G BY REACTION IN SOLUTION

The following experimental procedure is representative of those used in the successful preparation of the amide-ester resins by the solution method.

> To a solution of 5.96 g (0.05 mol) of 2-amino-2-ethyl-1,3-propanediol and 0.09 g Ionol in 75 ml DMF was added 6.58 g (0.065 mol) of triethylamine. The mixture was vigorously stirred in an ice-salt bath while a solution of 23.06 g (0.26 mol) of acryloyl chloride in 20 ml of toluene was added over a period of 30 minutes.

The mixture was then stirred continuously for 20 hours under nitrogen atmosphere. The solid amine hydrochloride which formed was removed by filtration and the solution was con- centrated with a rotary evaporator. The residue was washed with 75 ml of saturated sodium bicarbonate and extracted with three 50-ml portions of chloroform. The product was isolated by evaporating the chloroform, affording 12.5 g of A-G resin; 89% of the theoretical yield. The infrared spectrum of this resin is shown in Figure 5.
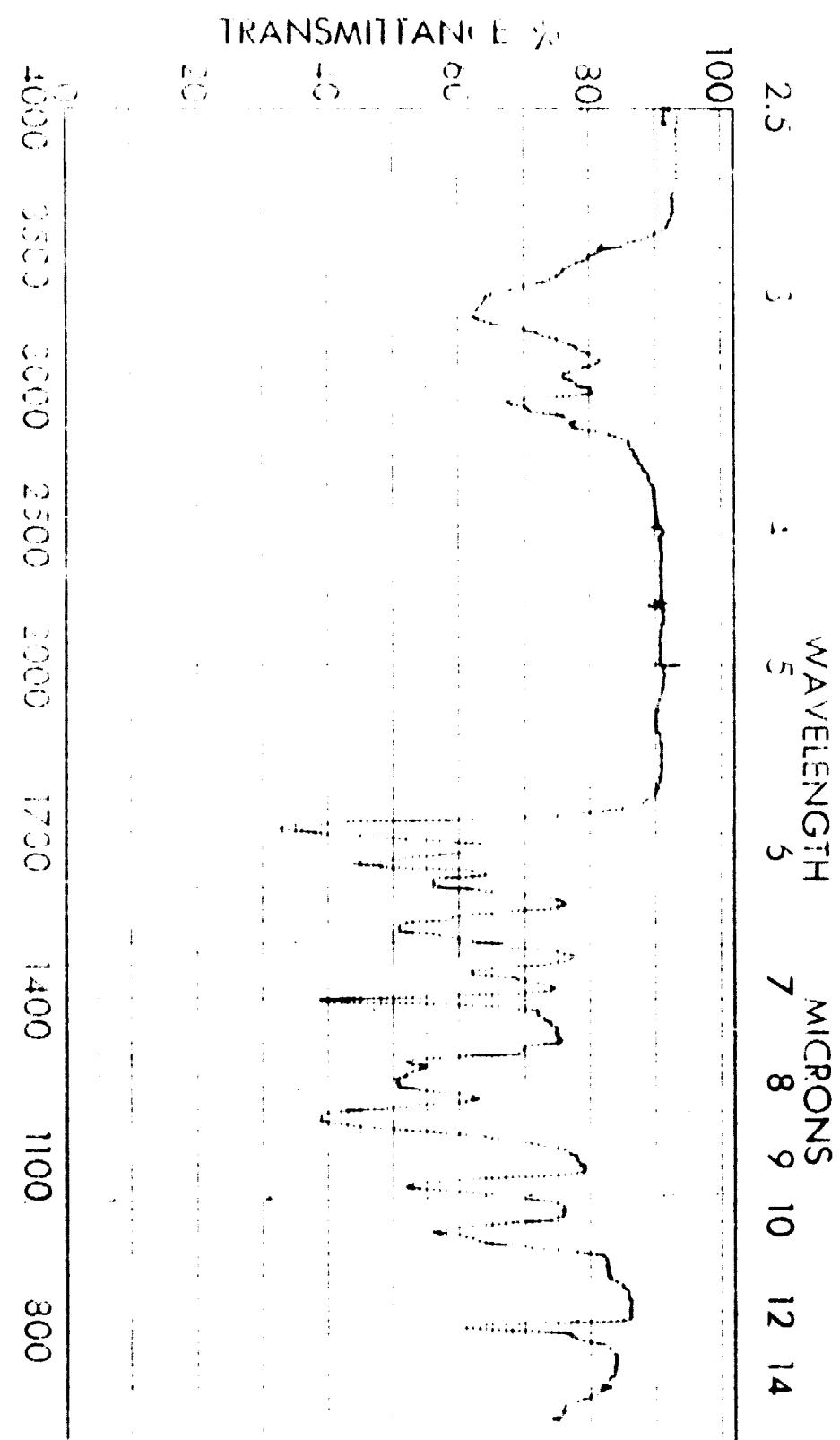
Figure 3. Infrared Spectrum of A-G Resin-Interfacial Method

TRANSMITTANCE %

100

80

60

30

20

10

WAVELENGTH MICRONS

2.5   3   4   5   6   7   8   9   10   12   14

FREQUENCY CM⁻¹

4000   3500   3000   2500   2000   1700   1400   1100   800
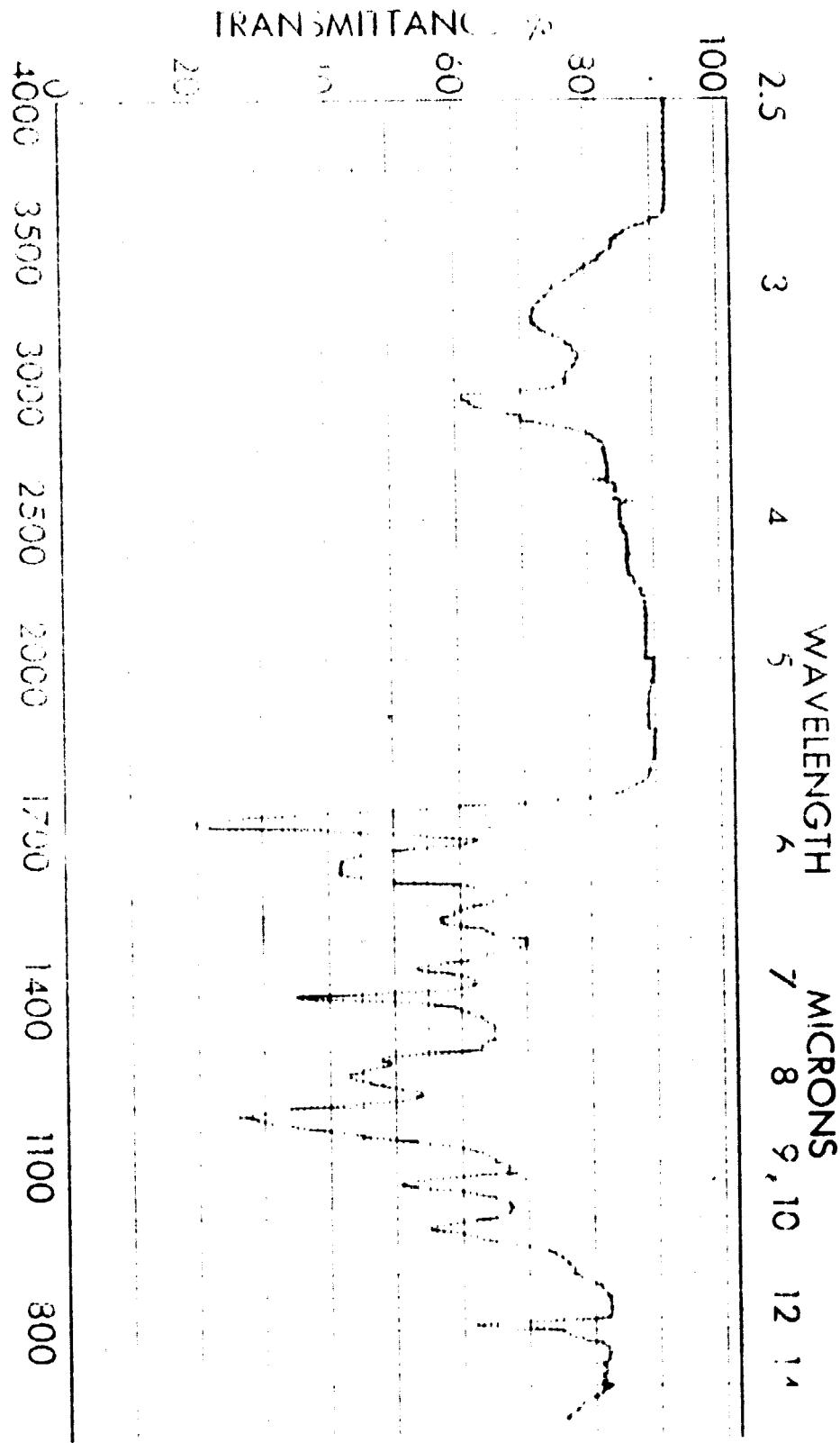
Figure 5.   Infrared Spectrum of A-G Resin-Solution Method

REFERENCE

1.   Cagle, Charles V., "Testing Adhesives.
     Adhesives Bonding Techniques and Applications,
     McGraw Hill, 1968, pp. 174-176.