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EXPLORATORY RESEARCH ON NOVEL AMBIENT TEMPERATURE CURING TECHNI--ETC(U)

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N00019-78-C-0169

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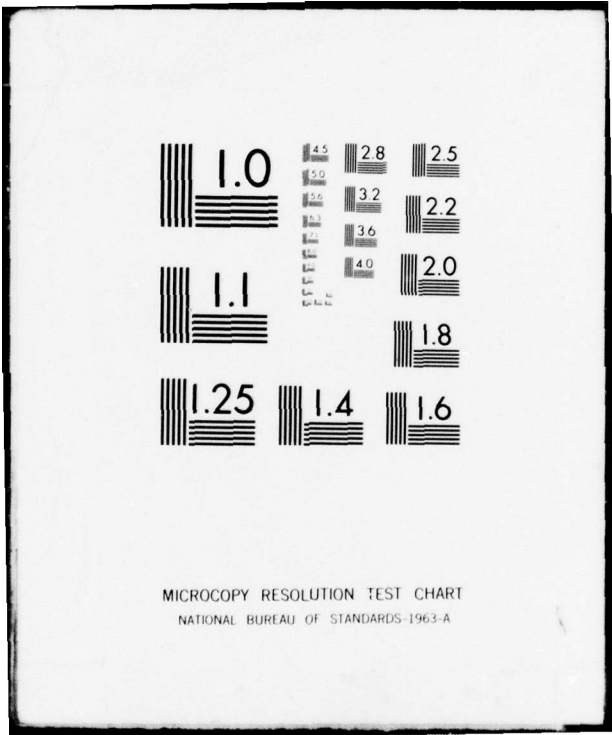
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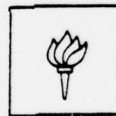
Walter Brenner
Principal Investigator

NYU/DAS 79-07

FINAL REPORT

APRIL 1979

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SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER 5-259-380
4. TITLE (and Subtitle) EXPLORATORY RESEARCH ON NOVEL AMBIENT TEMPERATURE CURING TECHNIQUES FOR ADHESIVES, SEALANTS AND LAMINATES.		5. TYPE OF REPORT & PERIOD COVERED FINAL REPORT-2/28/78-2/27/79
7. AUTHOR(s) 19 WALTER/BRENNER		6. PERFORMING ORG. REPORT NUMBER 14 NYU/DAS-79/07
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Applied Science/New York University 26-36 Stuyvesant Street (Barney Bldg.) New York, New York 10003		8. CONTRACT OR GRANT NUMBER(s) 15 N00019-78-C-0169
11. CONTROLLING OFFICE NAME AND ADDRESS Commander, Naval Air Systems Command Department of the Navy Washington, D.C. 20361		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS AIR-5163D2/JJG Ser 27
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) 12 83p.		12. REPORT DATE 11 APR 1979
16. DISTRIBUTION STATEMENT (of this Report) "APPROVED FOR PUBLIC RELEASE; DISTRIBUTION UNLIMITED" 9 Final rept. 28 Feb 78-27 Feb 79		13. NUMBER OF PAGES 81
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		15. SECURITY CLASS. (of this report) UNCLASSIFIED
18. SUPPLEMENTARY NOTES		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) NOVEL AMBIENT TEMPERATURE CURING TECHNIQUES FOR ADHESIVES, SEALANTS AND LAMINATES; AMBIENT TEMPERATURE CURING METHODS; LOW TEMPERATURE CURING EPOXIES WITH HIGH TEMPERATURE SERVICE PROPERTIES; ELECTRON BEAM RADIATION; FLASH POLYMERIZATION; INTERFACIAL POLYMERIZATION AND ANAEROBIC CURES.		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The performance properties of thermosetting polymer systems which are cured with the application of heat and pressure generally surpass those obtained with ambient temperature cures for the same systems. This report describes a program of research and development comprising the exploration and study of selected novel ambient temperature curing techniques with the goal of obtaining performance characteristics equaling or surpassing those achieved with conventional heat/pressure type cures. The specific room temperature curing methods experimentally investigated included electron beam radiation; flash polymerization;		

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ABSTRACT

The performance properties of thermosetting polymer systems which are cured with the application of heat and pressure generally surpass those obtained with ambient temperature cures for the same systems. This report describes a program of research and development comprising the exploration and study of selected novel ambient temperature curing techniques with the goal of obtaining performance characteristics equaling or surpassing those achieved with conventional heat/pressure type cures. The specific room temperature curing methods experimentally investigated included electron beam radiation; flash polymerization; interfacial polymerization and anaerobic cures. Some experiments were also carried out on room temperature curing epoxy polymer systems with high temperature service capabilities.

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I. INTRODUCTION

Nonmetallic materials such as adhesives, sealants and laminates are being increasingly utilized for the more cost effective construction of components of interest to the Naval Air Systems Command. Selected thermosetting organic polymer systems with or without fibrous reinforcements and/or fillers are generally preferred for these applications because they can provide the performance needed for the frequently severe anticipated service conditions when properly processed. More specifically, two component polymer systems comprising a base resin and a catalyst or curing agent which are reacted together, usually at elevated temperatures and pressures, either per se or mixed with reinforcing fibers, fillers, etc., are used. Autoclaves, high pressure presses, large ovens and other types of expensive and energy intensive equipment are generally employed for their fabrication into useful products. These processing requirements severely limit the employment of such polymer systems in situations where such equipment is not economically or technically viable such as for the production of a small number of parts with large, complex surface areas or field repair of damaged components.

Ambient temperature cures represent a potentially most attractive alternative to the present processing practices, especially so if they can be accomplished with readily attainable contact or vacuum pressures. Advantages include less equipment investment; simplified fabrication of both new parts and, where modifications or repair of old ones is indicated, amenability to processing shapes which by virtue of their large size and/or complex contours cannot be readily accommodated in generally available press or autoclave equipment; energy savings. The present state of the technology

for curing polymers at room temperature as practiced by processors today has, however, lagged behind that used with conventional heat/pressure cures which are now the choice for producing high performance nonmetallic components.

Recently, a number of new technical developments have been realized which could substantially enhance the potential of room temperature curing techniques by upgrading the quality and performance of thusly cured polymer systems. This report describes a program of research and development comprising the exploration and study of selected novel ambient temperature curing techniques. Their use could result in cured polymers with performance characteristics equaling or surpassing those achieved with conventional heat/pressure cures. The specific ambient temperature curing methods investigated experimentally include high energy ionizing electron beam radiation; flash polymerization; anaerobic polymerization and interfacial type polymerizations. Some experiments were also carried out on the development of room temperature curing polymer systems with high temperature service capabilities. The results obtained are critically reviewed and recommendations are made for additional investigations in this area of polymer processing.

II. AMBIENT TEMPERATURE CURING TECHNIQUES FOR THERMOSETTING ORGANIC POLYMER SYSTEMS

Many thermosetting organic polymer systems were recognized to be amenable to cures at ambient temperatures rather early in their technical development. Unsaturated polyester resins were among the first whose room temperature curing capabilities were deliberately utilized. These polymers are cured with free radicals produced by the decomposition of peroxide catalysts, heat or radiation¹⁾. Since the most commonly used organic peroxides are stable at ambient temperatures, the formation of a suitable number of free radical requires the addition of energy in forms such as heat, light or radiation. Chemicals known as 'accelerators' or 'promoters' have also been developed which facilitate the decomposition of organic peroxides at ambient temperature and initiate the curing process. Quite a number of specific catalyst and accelerator combinations are being successfully employed to polymerize the generally initially liquid resins into the solid state at ambient temperatures. Radiation cures and the like have thus far not been industrially developed.

The more important industrial accelerators are cobalt and vanadium compounds such as the naphthenates or octoates, tertiary amines and quaternary ammonium salts.¹⁾ Cobalt naphthenate or octoate are typically used in conjunction with ketone peroxides, hydroperoxides and peroxyester catalysts. Amine accelerators such as dimethyl amine find utility together with diacyl peroxides, especially benzoyl peroxides. Hydroperoxide catalysts are widely reported to work well with quaternary ammonium salts. Unsaturated polyester resins which are cured at room temperature with such catalyst/accelerator combinations, generally exhibit physical and chemical properties which fall short of those obtained with heat curing compositions. Also

polyester resins compounded with ambient temperature cure catalyst/accelerator systems tend to have pot life limitations which restrict their utility for some processing techniques such as for example, fiber reinforced prepreg materials unless refrigerated.

Epoxy resins which are probably the most versatile group of organic thermosetting materials in use today, can be cured at both ambient and elevated temperatures with curing agents such as amines, anhydrides and Lewis acids.²⁾³⁾ The amines can be further divided into aliphatic amines, amine adducts, heterocyclic amines, polyamides, aromatic amines, etc. The popularity of the aliphatic amines and polyamides is due to their ability to effect cures at ambient temperatures quickly and effectively. They offer relatively short working lives after mixing with the epoxy resin -- about 30 minutes to several hours at room temperature depending on amine, batch size, etc. -- but may require anywhere from four to seven days cure at ambient temperature to attain optimum properties. These classes of room temperature curing agents do not provide maximum strength properties, corrosion resistance and high temperature properties compared to the results achieved with heat curing aromatic amine or anhydride curing agents.

Other thermosetting organic polymer systems whose room temperature curing characteristics have been of interest include the phenolics, polyimides, silicones and polyurethanes. As is well known, phenolic resins were the first thermosets to be industrialized. The phenolics are known for their superior heat resistance, high rigidity, good thermal insulating properties, dimensional stability and chemical resistance.⁴⁾ Processing requires the use of catalysts, heat and pressures. No practical ambient room temperature curing systems have been developed.⁴⁾

The polyimides exhibit very high thermal stability, good mechanical strength properties, chemical resistance and quite remarkable dimensional stability. They generally require elevated temperatures and moderate to high pressures for cure. Processing to maximum performance characteristics may require exposure to a number of successively higher temperature conditions. The polyimides are relatively new materials and their preparatory as well as processing technology still remain to be optimized.

Recently modified polyimides have been prepared which can be cured by a free radical mechanism. Experiments indicate that at least some of these new polymers should have the capability of at least initial cure at ambient temperatures. A number of curing techniques should be evaluated experimentally for that purpose.

Silicone resins feature high heat resistance, low water absorption, good weatherability, superior dielectric properties and a high degree of stability in diverse and demanding environments.⁴⁾ Mechanical strength properties are however, inferior to those obtained with other thermosetting polymers such as the epoxies, polyimides, polyester, etc. Silicones can be cured at either elevated or ambient temperatures. A number of curing mechanisms have been investigated. With silicone adhesive/sealants for example, all of the curing reactions can be made to take place at the ends of the polymer chains.⁵⁾ These may be reactive groups such as hydroxyls or vinyls which react with a cross linking agent or catalyst to produce cured polymers. Both one and two component silicone polymer systems capable of room temperature cures have been developed.

One part room temperature curing silicones are classified by the type of product that is evolved during cure with various types of cure systems, e.g., acetic acid, oxime, alcohol or acetamide. The acetic acid cure systems are

the least expensive and the most widely used.⁵⁾ They have been developed to the point where they are formulated as single package systems which require no mixing before use and have long term storage stability.

Either a condensation or addition type cure mechanism can be employed for two part silicone polymer systems comprising a base polymer and a curing agent containing catalyst, cross-linkers or both. The condensation types two part silicones are similar to the one part silicones discussed above. Addition type cures give polymer products with superior heat stability, excellent corrosion resistance and minimum shrinkage because no volatiles are generated during cure. Adhesion to various substrates needs some improvements. The properties of addition type two part silicones are generally improved by a heat treatment.

The polyurethanes feature remarkable versatility in molecular design and compounding particularly for adhesives, sealant, encapsulants and also both rigid and flexible cellular materials.⁶⁾ Isocyanates containing the highly active and unsaturated $-N=C=O$ group react readily with a great many different compounds and can also react with themselves. Reactions can take place with most any compound containing hydrogen that is replaceable by or alkaline metal such as sodium as well as a multitude of other types of compounds whose hydrogen atoms are not readily replaced by sodium.⁷⁾

Reactions with compounds containing the $-NH$, $-OH$, $-CH$ and $-SH$ groups and miscellaneous active hydrogen compounds are well known as are reactions with unsaturated materials, dimerizations and trimerizations. Polyester and polyether glycols are among the most widely utilized materials for reactions with isocyanates to yield high molecular weight polymers. For applications where hydrolytic stability is required, polyethers are preferred.

A rather substantial body of literature has been built up on the preparation and formulation of one and two component polyurethanes for both ambient

and elevated temperature cures.⁶⁾ The kinetics of many of these systems have been studied in considerable detail. Some of the more widely used compositions which have been developed, are one component urethanes with blocked isocyanates which react on heating; moisture curable one component systems; and two component compounds in which the principal reaction is the formation of urethane groups by treatment of the hydroxyls of a polyether or polyester with isocyanate moities.

The problem of the reversion of polyurethane polymerization under certain humid conditions is a serious one which has as yet not been completely satisfactorily resolved. Improvements are needed in areas such as long term hydrolytic stability, organic solvent resistance and for elevated temperature service. This is especially the case for one component polyurethane compositions which are cured at room temperature. A considerable amount of R & D has been and continues to be carried out in order to achieve such enhanced polymer performance characteristics.

III. NOVEL AMBIENT TEMPERATURE CURING TECHNIQUES FOR ADHESIVES, SEALANTS AND LAMINATES

Currently employed room temperature curing techniques place definite limitations on the applicability of thermosetting organic polymer systems of interest to the Naval Air Systems Command. These limitations relate both to processing and performance. More specifically, they exhibit generally somewhat lower physical strengths, decreased resistance to chemicals including water, reduced thermal stability and electrical insulating properties, etc. than can be obtained with equivalent polymer systems after heat cures. Also the variability of specific properties measured on room temperature cure thermosetting polymer specimens tends to be significantly greater than that measured with heat cured test samples.

Processing limitations pertain both to working (pot) life and the size and/or shape of parts. The relatively short pot life, high exotherm and prolonged cure times needed to realize the best performance properties with polymers cured at ambient temperatures result in definite processing restrictions especially for parts with thick or variable thickness cross sections, large surface areas and/or complex contours. Cost effective fabrication of such parts would indicate the desirability of relatively long pot life for easy handling together with short gel and cure times for high productivity -- objectives which are difficult to achieve with the room temperature cure systems presently used in industry. Also skilled personnel is now employed to assure proper mixing and processing of room temperature curing two component systems. Techniques which will permit the use of unskilled labor, would obviously be desirable. On the other hand, as indicated above, room temperature cures have various important attractive features especially for the manufacture of a limited number of parts and field repair.

There exists therefore a very real need for exploring room temperature curing techniques further with the objective of overcoming the deficiencies of the presently practiced methods. This report describes a program of research and development comprising the exploration and study of selected novel ambient temperature curing techniques which could result in cured polymer properties with performance characteristics equal to or surpassing those achieved with thermal cures. The specific ambient temperature cure methods investigated experimentally include high energy ionizing electron beam radiation; flash polymerization; anaerobic polymerization and interfacial type polymerizations. Some experiments have also been carried out on the development of room temperature curing polymer systems with high temperature service capabilities.

IV. RADIATION CURING

A. Basic Technical Considerations

Radiation curing is defined as the polymerization or curing of organic polymer systems by subjecting them to radiation bombardment.⁸⁾ Most polymer systems cannot be cured readily by radiation and require chemical modifications. One type of radiation curable polymer system contains carbon-carbon double bonds and cures by a chain reaction mechanism known as addition polymerization. The amount of radiation to which polymers can be subjected to a polymerization and cure must be controlled and depends on their chemical composition. Exposure of polymer systems to excessively large amounts of radiation will result in degradation of their structure with resulting loss of their physical strengths and other properties.

Various forms of radiation have been employed for effecting the polymerization of organic polymers.⁸⁾ These comprise electromagnetic radiation such as gamma rays, ultraviolet rays, visible light rays, microwaves, RF waves and ultrasonic waves as well as particle radiation including electrons, alpha particles, beta particles and neutrons. For a continuous manufacturing process the three most widely employed forms of radiation are accelerated, i.e. high energy electrons, radioisotopes and ultraviolet light. This choice is based on considerations such as economy of operation; penetrating ability; ability to activate the entire volume of resin; obtainable dose rates (which control the rate of curing); residual radioactive contamination; shielding requirements and applicability to production operations.

Gamma radiation derived from isotopes such as cobalt 60 or cesium 137, although still considered by some to be a new process, has been in commercial use for at least a quarter of a century. At present, sterilization

of medical products especially disposables, is a major industrial application. Both electron beam (EB) and ultraviolet (UV) radiation sources are relatively new to the industrial production environment even though they have been used extensively in research laboratories and pilot plants for the better part of the last two decades.⁸⁾ EB radiation is being employed extensively in such industrial applications as the cross linking of thermoplastic wire and cable insulations and also plastic packaging films. UV radiation is finding applications in the coatings field and related areas.

The latest and as yet largely unexplored radiation technique is said to make a novel use of the electromagnetic spectrum to deliver energy in a pulsed mode with high peak powers. It utilizes xenon lamps and is called flash polymerization.⁹⁾ This method will be discussed in a later section of this report. Microwave curing is recognized as still another radiation curing method of considerable merit especially for curing elastomers and some fiber reinforced plastics. As it is not an ambient temperature curing technique, it will not be discussed further here.

The two radiation sources of greatest interest for curing thermosetting polymer systems in configurations where cross section thickness greater than a few mils required are high energy electron beams (EB) from accelerator machines and cobalt 60 (CO-60) from isotopes.³⁾ Table #1 compares the properties of these two radiation sources. Electron beams have emerged as the generally preferred choice even though cobalt-60 radiation has greater penetrating power. Specific advantages of EB radiation include higher dose rate capability for minimum cure times and thus higher throughputs, constant radiation strength, low cost of delivered radiation and no replenishment requirements.

TABLE #1. COMPARISON OF HIGH ENERGY ELECTRON BEAM AND COBALT-60 RADIOISOTOPE RADIATION SOURCES

RADIATION SOURCE	CHARACTERISTICS
- Radioisotopes	<ul style="list-style-type: none"> - high reliability - continuous radiation (cannot be turned off) - gradual loss of strength - requires replenishment - high cost of delivered radiation - delivers low dose rates
- high energy electrons	<ul style="list-style-type: none"> - periodic maintenance required - radiation can be turned on and off - constant strength - no replenishment required - low cost of delivered radiation - delivers high dose rates

EB curing has likewise definite advantages over conventional UV curing techniques. They include substantially greater and more controlled depth of the penetration of the radiation, higher dose rate capability, faster cure times and insensitivity to opaque fillers, pigments, etc. On the other hand the investment cost for installed EB accelerator equipment is very much larger than that needed for conventional UV lamp installations. The price of cobalt-60 is controlled by government regulations. The cost of shielding a cobalt-60 installation for providing adequate safety to operating personnel are considerable. EB processing systems can usually be employed for a variety of curing tasks while UV and also cobalt-60 installations are generally designed with a specific application in mind.

Accelerated electron beam radiation deposits energy directly in the organic polymer and given a sufficient amount of energy deposited, curing can occur in a few seconds even at room temperatures. The penetration of such electrons is limited however, and any material placed between the radiation source and the polymer will shield the polymer. This limits the thickness of the organic material to be cured and also limits curing a line-of-sight process only.

The voltage (kinetic energy) of the high energy electron is important because it determines the depth to which it can penetrate a given material. For a specific voltage, the penetration is inversely proportional to the density of the material being bombarded. The voltage requirement of an electron beam accelerator used for an industrial process is therefore determined by the thickness and the density of the material to be cured. Electron energy is usually expressed in millions of volts (MEV) or thousands of volts (KEV). Table #2 lists the maximum penetration for a material of unit specific gravity with equal entrance and exit dosage as a function of the electron energy.

TABLE 2: MAXIMUM PENETRATION FOR A UNIT DENSITY MATERIAL WITH EQUAL ENTRANCE AND EXIT DOSAGE AS A FUNCTION OF ELECTRON ENERGY

<u>Electron, energy, MEV</u>	<u>Maximum penetration, mils</u>
0.75	90
1.0	125
1.5	185
3.0	370

"The quantity of required radiation relates to the amount of material to be cured -- the higher the current of the electron beam, the greater the amount of material than can be cured.⁸⁾ By analogy the amount of radiation used is related to the amount of catalyst used in thermal/chemical curing. 1 milliamperere of electron beam current equals 6.28×10^{15} electrons per second. Table #3 lists typical performance characteristics for a 3 MEV electron accelerator. The data show that a 1.0 specific gravity polymeric material could receive a dosage of 5 megarads while passing under the electron beam at a speed of 12 ft/min (2 foot scan) or 6 ft/min (4 foot scan). For a specific gravity 2.0 material, the penetration depth would be 185 mils and the absorbed dose conveyor speed as shown. Assuming that a dosage of 5 megarads, completely cures a 1.0 specific gravity material, the 3 MEV machine could completely cure an area measuring 12' x 2' x 0.370" thick in one minute.

TABLE # 3. 3.0 MEV ELECTRON BEAM ACCELERATOR SPECIFICATIONS

A. Conveyor speed vs. dosage for 100 cps and 12 m amps beam current
(Assuming 50% beam utilization efficiency)

<u>Absorbed dose (sp. grav. 1.0)</u>	<u>2 ft. scan</u>	<u>4 ft. scan</u>
1 megarad	60 ft/min	30 ft/min
2 megarad	30 ft/min	15 ft/min
5 megarad	12 ft/min	6 ft/min

B. Maximum penetration for unit density material, equal entrance and exit dosage

0.75 MEV	90 mils
1.50 MEV	185 mils
3.0 MEV	370 mils

The cost of electron beam curing at a 5 megarad dosage would be less than one cent per pound of polymeric raw material. This cost, which includes operator cost is based on the assumption that the accelerator will be used 4000 hours per year at a maximum production rate of the cured material. Considerable industrial experience with electron beam radiation curing of products such as thermoplastic wire insulation and packaging films shows that these cost estimates are realistic for a production situation and also that they compare quite favorable with those needed for conventional thermal/catalytic cures.

Many problems associated with such conventional thermal catalytic curing have been tolerated in the past for the production of high performance composites, adhesives, sealants, etc., because there was simply no other curing method available. Radiation curing promises the following specific very significant improvements:

- room temperature curing (eliminates thermal distortion of parts, oven equipment, etc.).
- very short cure cycles together with indefinitely long pot life.
- elimination of multiple sets of expensive tooling and facilities
- elimination of hazardous chemicals (e.g. catalysts, accelerators) and deleterious by products (noxious gases, residues)
- staged production (compounds can be cured in sections)
- automated production lines.

B. Experimental

Room temperature curing of adhesives, sealants, laminates, etc., with electron beam radiation has been discussed as offering a number of significant advantages over conventional thermal/catalytic curing techniques. This section describes exploratory investigations of radiation curing of selected thermosetting organic polymer systems and fiber reinforced thermosetting resin laminates at ambient temperatures.

A 3 MEV electron beam accelerator machine called the Dynamitron by its manufacturer, Radiation Dynamics, Inc. (Melville, L.I., N.Y.) was employed as the source of the ionizing radiation for the curing of the various polymeric materials and composites. This machine can irradiate up to 72" wide 0.37" thick unit density material at the 3 MEV level continuously on a moving belt type of conveyor or discrete carts which can be moved underneath the electron beam.

Measured quantities of selected radiation curable thermosetting polymer systems in the form of castings or uncured flat sheet lay-ups of glass fiber cloth reinforced resin bonded laminates were contained in or deposited onto suitably shaped high density polyethylene sheet supports. Casting compositions were formulated with a mineral filler to prevent the development of excessive exotherm during cure. The fiber reinforced resin lay ups contained about 70% by weight glass fibers. These assemblies were then tightly wrapped with strapping tape to maintain their configuration during handling, positioning and curing. The radiation polymerizable casting compositions and flat sheet lay-ups had approximate dimensions of 10" x 8" x 1/8". The candidate electron beam curing polymer systems did not contain any catalyst or accelerators.

The irradiations were all conducted at ambient temperatures and in the presence of air. The assemblies with the various test specimens were placed on a conveyor which moved underneath the beam of a 3 MEV Dynamitron electron beam accelerator located at the Radiation Dynamics, Inc. Service Center at Plainview, L.I., N.Y. This facility has a magnetic beam sweeping accessory that provides a uniform electron flux over a line width of 4 ft. A constant speed conveyor system carries the test assemblies through the line of electrons emerging from the horn of the machine so that uniform, large area irradiations can be obtained.

The Dynamitron operating conditions were 3 MEV and 25 milliamperes. With the conveyor moving at a speed of 30 feet per minute, the dosage rate was 2.5 megarads (Mrads) per pass through the beam. The exposure time of the various specimens to the radiation was in the order of a few seconds. Tables 4 and 5 and Figures 1, 2 and 3 summarize specific experimental conditions and typical test results. The strength properties of two typical radiation cured laminates are compared with those of peroxide cured laminates of the same composition in Table 5. The various temperature data were obtained after a 1 hour soak at the indicated temperature. The specific resins investigated were unsaturated polyesters and epoxy acrylates selected on the basis of their reported capability to withstand high service temperatures.

TABLE 3: STRENGTH PROPERTIES OF SELECTED RADIATION CURED THERMOSETTING POLYMER CASTINGS AT AMBIENT AND ELEVATED TEMPERATURES

A. Aluminum filled polyester resin castings (32 volume % alumina)

Koppers 3700-50 polyester resin, 8 MR irradiation dosage

Test Temperature, °F	Flexural Strength, PSI		Flexural Modulus, PSI X 10 ⁵	
	No post cure	16 hour post cure at 350 °F	No post cure	16 hours post cure at 350°F
RT	6,520	6,730	7.05	9.14
150	2,860	3,420	2.06	2.71
250	1,810	2,060	0.94	1.04
330	1,230	930	0.36	0.42
400	540	670	0.30	0.36
500	-	260	-	0.45

Koppers 3700-50, 12 MR irradiation dosage

RT	7,100	8,500	7.45	10.13
150	3,250	3,400	2.34	2.92
250	2,050	1,980	1.06	1.02
330	750	816	0.49	0.54
400	1,080	510	0.60	0.47
500	690	320	0.70	0.56

TABLE 3 (Cont'd)

Test Temperature, °F	Flexural Strength, PSI		Flexural Modulus, PSI X 10 ⁵	
	No post cure	16 hours post cure at 350 °F	No Post cure	16 hours post cure at 350 °F
<u>Koppers 3700-50, 20 MR irradiation dosage</u>				
RT	6,740	7,580	8.05	11.67
150	3,520	3,840	3.14	3.82
250	2,460	2,910	1.63	1.42
330	1,150	1,010	0.61	0.48
400	730	630	0.52	0.53
500	640	520	-	-
<u>Koppers 7000, polyester resin, 8 MR irradiation dosage</u>				
RT	7,350	7,810	8.37	9.05
150	3,840	3,960	6.15	7.81
250	3,280	3,060	2.24	3.46
330	2,420	2,850	1.61	1.82
400	1,890	1,630	1.08	0.95
500	910	1,010	0.75	0.63
<u>Koppers 7000 polyester, resin, 12 MR irradiation dosage</u>				
RT	7,280	7,650	8.51	8.63
150	4,110	4,246	5.38	6.27
250	3,420	3,280	4.71	4.13
330	2,380	3,020	3.62	2.75
400	1,620	1,470	1.25	1.60
500	730	940	0.80	1.04
<u>Koppers 7000 polyester resin, 20 MR irradiation dosage</u>				
RT	7,420	7,260	8.16	8.73
150	5,310	4,680	5.92	4.67
250	4,160	3,480	4.26	4.58
330	1,830	2,150	2.81	3.42
400	1,320	1,880	1.46	1.72
500	790	940	1.08	1.18
<u>Vibrin 136 A polyester resin, 8 MR irradiation dosage</u>				
RT	6,930	6,810	8.23	8.30
150	5,890	6,340	7.84	7.91
250	4,260	4,130	4.62	5.13
330	4,140	4,340	2.07	2.24
400	1,850	2,070	1.28	1.47
500	1,080	1,240	0.95	1.14

Table 3 (Cont'd)

Test Temperature °F	Flexural Strength, PSI		Flexural Modulus, PSI X 10 ⁵	
	No post cure	16 hours post cure at 350 °F	No Post cure	16 hours post cure at 350 °F

Vibrin 136 A polyester resin, 12 MR irradiation dosage

RT	6,540	7,260	8.05	8.17
150	6,310	5,440	7.81	8.22
250	3,740	3,890	7.82	8.06
350	2,540	2,480	1.80	1.73
400	1,820	1,860	1.53	1.41
500	1.130	1,080	0.90	1.02

Vibrin 136 A polyester resin, 20 MR irradiation dosage

RT	7,050	6,840	8.11	8.08
150	6,240	6,580	7.92	7.83
250	4,310	4,080	7.34	7.28
350	2,840	2,540	3.08	2.10
400	2,070	2,080	1.78	1.16
500	1,030	1,180	1.15	0.95

Vibrin 115 polyester resin, 5 MR irradiation dosage

RT	4,340	4,850	7.05	7.64
150	4,210	4,920	6.90	7.82
250	3,680	4,920	6.90	7.82
350	3,680	3,890	6.85	8.41
400	1,380	1,350	2.77	2.72
500	1,120	1,140	1.34	1.20
	1,060	980	1.06	1.12

Vibrin 115 polyester resin, 12 MR irradiation dosage

RT	4,610	4,560	10.15	11.6
150	4,640	4,350	9.65	8.95
250	3,290	3,540	5.9	4.15
350	1,960	2,080	1.81	1.86
400	1,090	1,160	1.16	1.12
500	960	780	0.84	0.97

Vibrin 115 polyester resin, 20 MR irradiation dosage

RT	4,730	4,810	9.13	3.05
150	4,380	4,520	8.25	7.16
250	4,290	4,300	6.18	5.48
350	3,030	2,810	1.30	1.45
400	1,810	1,630	1.24	1.38
500	1,120	980	0.65	0.90

Selectron 5016 polyester resin, 6 MR irradiation dosage

RT	4,210	4,460	9.05	8.24
150	4,300	4,240	7.30	7.95
250	3,290	3,540	5.90	6.23
350	1,960	2,080	1.81	1.86
400	1,310	1,260	1.21	1.08
500	1,020	930	0.85	0.92

TABLE 3 (Cont'd)

Test Temperature °F	Flexural Strength, PSI		Flexural Modulus, PSI X 10 ⁵	
	No post cure	16 hrs. post cure at 350°F	No Post cure	16 hrs. post cure at 350°F

Selectron 5016 polyester resin, 12 MR irradiation dosage

RT	4,520	4,860	8.35	8.06
150	3,630	3,520	8.26	7.36
250	2,050	2,140	4.35	3.80
350	1,760	1,920	1.24	1.18
400	1,210	1,080	1.04	0.95
500	980	870	0.88	0.72

Selectron 5016 polyester resin, 20 MR irradiation dosage

RT	4,720	5,030	9.25	9.64
150	3,260	4,020	8.10	6.28
250	2,120	2,180	3.80	4.13
350	1,430	1,380	2.85	2.46
400	1,020	1,030	1.35	1.82
500	910	820	1.10	0.98

B. Alumina Filled Epoxy Acrylate Castings (30 volume % alumina)Epocryl U12 epoxy acrylate resin, 18 MR irradiation dosage

RT	9,640	10,070	8.92	8.84
150	10,100	9,870	8.10	7.84
250	8,650	8,186	6.32	5.48
350	6,340	5,840	1.57	2.04
400	2,130	2,410	1.24	1.61
500	1,160	1,420	1.06	0.95

Epocryl U12 epoxy acrylate resin, 24 MR irradiation dosage

RT	10,140	10,080	9.15	7.84
150	8,310	9,120	8.30	8.08
250	6,160	7,460	5.16	7.14
350	5,180	5,060	1.48	1.83
400	2,340	2,620	1.20	1.15
500	1,050	1,140	0.92	0.88

Epocryl U12/TAC epoxy acrylate resin blend (80/20 wt ratio), 24 megarad irradiation dosage

RT	8,350	7,980	9.05	8.90
150	8,180	8,240	8.63	8.75
250	6,070	6,480	6.52	5.18
350	4,140	5,620	4.10	2.35
400	1,300	1,120	1.26	-
500	960	1,050	1.00	0.83

Table 3 (Cont'd)

Test Temper-
ature
°F

Flexural Strength, PSI
No post | 16 hours post
cure | cure at 350 °F

Flexural Modulus, PSI X 10⁵
No Post | 16 hours post cure
cure | at 350 °F

C. Alumina Filled Urethane Acrylic Castings (33 volume % alumina)

Uvithane 783/VP urethane acrylic/vinyl pyrrolidone blend (80/20 wt ratio)

RT	4,320	4,410	5.12	5.34
150	4,100	3,970	3.42	2.75
250	2,040	1,860	0.95	0.86
350	780	810	-	-

Uvithane 893/VP urethane acrylic/vinyl pyrrolidone blend (80/20 wt ratio)

RT	3,680	3,740	4.83	5.10
150	3,120	3,240	2.80	3.10
250	1,380	1,260	0.83	0.72
350	540	610	0.45	-

TABLE #4: STRENGTH PROPERTIES OF SELECTED RADIATION CURED THERMOSETTING POLYMER LAMINATES AT AMBIENT AND ELEVATED TEMPERATURES

Processing Conditions	Epocryl 12	(181 Volume A Cloth Reinforcement) Epocryl 12 plus 20% TAC	Vibrin 135A	Koppers 3700-50	Koppers 7000
Dose per pass, MR	6	2	2	2	2
No of passes used	4	12	12	12	12
total dosage, MR	24	24	24	24	24
Wt% resin (average)	31	30.7	28.6	27.9	33.6
Barcol hardness, front side	71-75	72-80	72-81	74-81	70-76
" " back side	80-85	65-72	68-72	78-80	65-75
Laminates thickness, inches	0.108 - 0.137	0.107 - 0.128	0.103 - 0.121	0.092 - 0.106	0.108 - 0.130
<u>Compressive Strength, PSI</u>					
RT	31,000	45,080	27,060	37,200	32,800
270	24,300	23,600	21,340	25,070	27,600
350	24,600	22,580	21,610	20,680	20,450
420	21,500	12,810	16,540	20,680	11,100
500	14,600	14,800	15,200	6,200	10,700
<u>Flexural strength, PSI</u>					
RT	60,400	71,960	54,600	70,810	66,400
270	40,810	52,300	36,840	51,610	50,240
350	37,600	42,940	41,150	39,480	29,480
420	38,200	13,890	38,510	19,360	19,860
500	24,460	10,640	39,260	17,240	16,130
<u>Flexural Modulus, PSI x 10⁻⁶</u>					
RT	3.20	3.31	3.23	3.34	3.15
270	2.69	3.02	2.72	3.25	2.68
350	2.59	2.28	2.20	2.10	2.34
420	2.84	1.65	1.76	1.64	1.29
500	2.52	1.74	1.41	1.24	1.18

TABLE 4: (Cont.d)

Processing Conditions	(181 Volume A Cloth Reinforcement)				
	Epocryl 12	Epocryl 12 plus 20% TAC	Vibrin 135A	Koppers 3700-50	Koppers 7000
<u>Tensile Strength, PSI</u>					
RT	52,000	64,300	42,100	57,660	45,720
350	41,600	49,710	36,240	41,380	30,150
420	23,800	16,530	19,650	24,430	14,840

TABLE 5: COMPARISON OF STRENGTH PROPERTIES OF RADIATION AND PEROXIDE CURED LAMINATES OF THE SAME COMPOSITION

(Radiation cure: 24 megarads at 2 megarads per pass at room temperature, contact pressure
 Peroxide cure: 1% benzoyl peroxide catalyst; 1 hour at 250°F; 85 psi)

	<u>Radiation Cured Epocryl U12/TAC</u>	<u>Peroxide cured Epocryl U12/TAC</u>
Wt resin average	30.7	28
Barcol hardness, front side	72-80	73-76
Barcol hardness, back side	65-72	82-85
laminare thickness, inches	0.107-0.128	0.125-0.135
<u>Compressive Strength, PSI</u>		
RT	45,080	48,260
270	23,600	25,340
350	22,580	21,850
420	12,810	13,080
500	14,800	16,150
<u>Flexural Strength, PSI</u>		
RT	71,960	73,810
270	52,300	51,740
350	42,940	43,060
420	13,890	15,100
500	10,640	9,480
<u>Flexural modulus, Psi x 10⁻⁶</u>		
RT	3.31	3.45
270	3.02	3.12
350	2.28	2.30
420	1.65	1.68
500	1.74	1.60
<u>Tensile Strength, PSI</u>		
RT	64,300	63,800
350	49,710	47,650
420	16,530	18,100

These and other similar casting and laminate experiments show clearly that unsaturated polyester and epoxy acrylate resins can be cured quite effectively by exposure to high energy electron beam ionizing radiation. The following specific advantageous processing characteristics can be ascertained for this type of cure:

1. infinite pot life for resin system; no catalysts or accelerators required; no mixing needed
2. high speed cure at ambient temperatures: minutes compared to hours for conventional thermal cures
3. no post cure required to obtain elevated temperature performance equivalent to that realized with thermal cures; freedom from thermally induced stresses
4. contact pressure gives good physical strength properties at ambient temperatures
5. material saving; no catalyst or accelerators needed
6. energy saving; energy is applied quickly only where needed in contrast to thermal cures where energy is wasted heating the entire inside volume of an oven for prolonged time periods
7. equipment saving; no ovens or similar heating equipment required
8. high productivity due to fast cure times.

The main limitations for electron beam radiation curing are seen to be as follows:

1. special types of resins may be required, e.g. free radical type of cure mechanism preferred.
2. equipment investment for electron beam accelerator high and must be justified on greater productivity cost effectiveness
3. line-of-sight-curing limitation
4. curing thickness limitation based on energy level of the electron beam employed.

Consideration of both the positive and negative aspects of radiation curing recommends this technique especially for high volume production. Further experiments should therefore be carried out on the reformulation of other thermosetting resin systems of interest to the Naval Air Systems Command

so that they can be processed by irradiation curing. Preliminary recent studies are showing for example, that acrylic modified polyimides and urethanes can be cured by exposure to electron beam radiation. Successful reformulation of such resin systems would greatly enhance the scope and therefore the applicability of this novel curing method.

V. FLASH POLYMERIZATION

It has recently been deemed of considerable interest to enhance the performance capability of UV curing techniques which because of limited penetration depth are mainly employed for curing coatings. Application of concepts such as pulsed xenon lamp radiation or chemically sensitized so called 'visible light' radiation techniques is being studied for curing organic polymers with greater cross section thickness than can be achieved with conventional UV lamps both in this country and abroad.⁹⁻¹⁹⁾

The high peak intensity output of suitably designed pulsed xenon lamps has been proposed as being particularly effective for obtaining deeper penetration of organic polymeric materials and achieving cures. Also the continuous energy spectrum emitted by such lamps has been stated to allow a wider range of photoinitiators with the possibility of lowering costs and making selection of candidate materials less critical. Specific xenon lamp systems proposed for curing thermosetting polymer, include the Xenon Corporation's (Wilmington, Mass) "flash polymerization,"^{9),10)} Berkey Technical Company's (Woodside, N.Y.) "Ascor Pulse Cure"¹¹⁾ and the Hildelbrand Company's (Oberboihinge, W. Germany) "IST" process.¹²⁾ The high intensity, short duration energy flashes produced by pulsed xenon gas discharge lamps when electrical energy stored in a capacity is discharged through the lamp, reportedly enhances penetration depth significantly.

This section of the report is concerned with a brief exploratory study of the Xenon Corporation's flash polymerization process which has been advocated for the rapid curing of polymers in thickness from a few mils to 3/4" and more.^{9),10),17),18)} The most dramatic claims for this curing technique relate to "thick, opaque materials that do not respond effectively to other radiation processes." According to Xenon Corporation who state that the nature of the

curing mechanism involved is far from fully understood, the prime variables of this process are part configuration including thickness, energy density, pulse recurrence frequency, pulse duration and the characteristics of the emitted spectrum.

The Xenon "flash polymerization process is stated to require "tuning" of the energy emitted by the lamps to the absorption characteristics of the chemical system under consideration for achieving optimal cures.^{9),17)} It differs from other methods such as the "Ascor Pulse" and "IST" processes in that intense heat as well as light is produced with much higher pulse intensity levels, lower pulse time durations and an energy spectrum which covers a very wide range of wavelengths.

Xenon Corporation claims that with their equipment, electrical energy can be efficiently converted to energy in the electromagnetic spectrum producing a very broad radiation spectrum at high peak powers (i.e. 10^5 to 10^9 watts)⁹⁾ The high peak powers are stated to help overcome the effects of the inverse square law governing depth of penetration. Flash polymerization can therefore provide the full electromagnetic spectrum at high peak powers to achieve rapid photo and thermal reactions both of which are involved when curing polymers according to Xenon. For chemically unsaturated polymeric materials, etc. "the UV energy from the high intensity pulses is captured by the photoinitiator in the chemical system (if one has been added) and creates free radicals which propagate the polymerization (curing) reaction."⁽¹⁰⁾ In other systems "the infra-red portion of the lamp energy output initiates and sustains the thermal reaction... the power spike, because it is delivered in a short, rapid pulse, does its work before the polymeric material can deteriorate."⁽¹⁰⁾

A prototype Xenon lamp system has been reported to have successfully cured flat, 12 ply laminates of Cordopreg UVFR7581, a fiberglass reinforced polyester prepreg tape.¹⁰⁾ The curing condition was said to be 1 minute at an initially ambient temperature. Three-quarter inch thick slabs of the same prepreg

material were said to have been cured in only 4 minutes. Twelve plies of Hexcel F670 epoxy novolac prepreg were cured in 8 minutes to produce a 1/8" thick laminate with a Barcol hardness of 75. Shell Chemical Co's Epon 828 resin and FP7A hardener have been employed to impregnate 12 plies of 181 style fiberglass cloth. The assembly is said to have been cured via Xenon flash polymerization in 9 minutes to a 75 Barcol hardness. Also 12 plies of Hexcel F224-6 phenolic prepreg have been cured in about 6 minutes. Other examples cited by Xenon Corporation include successful cures of polyurethane coatings and RTV silicone rubbers in short time periods.¹⁰⁾ These test reports were deemed impressive enough to warrant an exploratory study of flash polymerization.

The flash polymerization experiments were carried out with equipment designed and built by the Xenon Corporation. The specific unit used was a one kilowatt (1KW) polymer flash polymerization laboratory unit called Model 564. This unit delivers high intensity pulsed white light which encompasses the full spectrum from the infrared region (11,000 A°) to the ultraviolet region (2200 A°). The amounts of UV/IR emitted are related to the mode of operation especially the output voltage (DC). As shown in Fig. #4, in general, the higher the DC Voltage output, the greater the quantity of UV light.

The Model 564 flash polymerization laboratory unit has the following specifications: (a) maximum flash voltage 3000 volts, D.C.; (b) maximum switch energy per flash 125 watt-sec.; (c) pulse width (duration) 125 microseconds; (d) power output 1000 watts; (e) input power 230 volts AC 3 phase with 300 amps peak; (f) maximum flash rate 8 pulses per second; and (g) effective area available for curing approximately 3" x 3". Assuming the pulse duration is 125 microseconds and the maximum switch energy per flash 125 watt-seconds, the instantaneous energy output will be 10^6 watts. This instantaneous energy is called the "peak power" and represents the fundamental difference between conventional UV and

flash polymerization equipment. As noted above, it is the Xenon Corporation's claim that the high peak power (10^6 watts) which can be achieved with this pulsed flash mode of energy delivery which appears to be able to overcome the inverse square law governing the depth of radiation penetration. Also the infrared region of the emitted energy which will heat up the polymer sample which in turn will increase the rate of polymerization.

More specifically, the energy for polymerization is obtained with the Model 564 Xenon flash polymerization laboratory unit by the conversion of pulsed electrical energy to light using the system illustrated in Figures 5 and 6. This energy storage system permits the storage of electrical energy for predetermined delivery in controlled short pulses. The pulse shaping network controls the pulse rise time, width and fall time. The trigger control system activates the lamp when triggered from the master control. The stored electrical energy is discharged into the lamp at peak powers up to 1,000,000 watts when ignition occurs. The lamp then instantaneously converts the electrical energy to light at very high peak intensities. The resulting plasma generates electromagnetic energy with color temperatures ranging from 2,000 to 20,000 degrees Kelvin depending on pulse shape and lamp design. Heat buildup in the produce is said to be minimized because of the short time duration of the energy pulse.

This laboratory unit was used to explore the curing of various resin systems via flash polymerization. Preliminary qualitative experiments were conducted to ascertain such parameters as the distance between the polymer sample to be cured and the Xenon lamp; lamp pulsing rate and duration; lamp pulsing intensity and total energy usage; total exposure time, and waiting time, i.e. time before sample is examined after light exposure, and heat up of sample during exposure. A two component epoxy resin system comprising Shell Chemical Co's Epon 828 resin mixed with General Mill's Versamid V25 hardener (100/75 parts by wt) was used for the initial experiments. This resin

system which can be cured overnight at ambient temperatures, has been claimed to be capable of cure in about 60 seconds by flash polymerization. This resin mixture was poured into 2-1/2" diameter 1/2" high aluminum cups to a specified depth. The resin filled cups were then exposed to various flash polymerization conditions. Table 6 summarizes the results of some of these experiments.

These experiments showed that the cure of this twin component epoxy resin system can indeed be significantly accelerated by exposure to the flash polymerization. The cure time was found to depend on such variables as the distance of the polymer sample from the lamp and the pulse rate. Longer cure times caused foaming with hardening, probably due to excessive heat and exotherm development. In general, the curing conditions, especially time, were found to be rather critical for obtaining sound cured polymer samples. One interesting observation was that the cured epoxy resin samples exhibited initially rather low physical strengths. However, after about 1 to 1½ hours the physical strength was found to be substantially improved.

It was considered that the observed acceleration of the polymerization reaction could be related at least partially to the temperature increase of the polymer samples which occurred when they were exposed to the flash polymerization conditions described in Table 6. A simple experiment was carried out to verify this hypothesis. An aluminum dish without resin was exposed to the same conditions of flash polymerization. A copper-constantan thermocouple was affixed to the inside surface of the aluminum dish. Figure 7 records the temperature increase of this dish as a function of the flash polymerization exposure time. The data show that a temperature of approximately 260°F was reached after about 100 seconds of exposure. The temperature rise of the same type of a aluminum dish filled with 8 grams of the above specified epoxy resin mixture was similarly measured. The test data show a temperature rise to more than 300°F within 100 seconds. The results do strongly support the

TABLE 6: CURING RESULTS FOR TWO COMPONENT EPOXY RESIN SYSTEM BY FLASH POLYMERIZATION TECHNIQUE

SAMPLE SIZE/THICKNESS	DISTANCE (IN.)	EXPOSURE TIME SECONDS	PULSE RATE PPS	OUTPUT VOLTAGE	LAMP POSITION CONTAINER	RESULTS
8g/0.25"	3.0	60	8	2,200	Face Down Al dish	Surface start to hardening
"	"	75	"	"	"	Surface start to hardening
"	"	90	"	"	"	Surface start to hardening
"	"	105	"	"	"	Surface start to hardening
"	"	120	"	"	"	Hardened to 1/64" thick
"	"	150	"	"	"	All solidify, but no strength
"	"	105	"	"	"	Bottom start to hardening
"	"	120	"	"	"	Hardened foam
"	0.25	90	"	"	"	Hardened foam, little strength
"	4"	120	2	"	"	Hardened foam, little strength
"	4"	120	8	"	"	Hardened foam, little strength
"	4"	105	8	"	"	Hardened foam, little strength
"	4"	90	8	"	"	Surface starts to harden

- 1 From bottom of container to edge of lamp housing
- 2 Pulses per second
- 3 Face down means the light faces the sample directly; face up means the light passes through the aluminum container wall before reaching the sample.
- 4 Resin formulation; Shell Chemical Company Epon 828/General Mills Versamid V25; 100/75 parts by weight
- 5 Examined immediately after the light exposure
- 6 Epoxy resin sample was completely hardened in the aluminum dish after 1-1/2 hour dwell at ambient temperature.

TABLE 7: FLASH POLYMERIZATION CURING RESULTS FOR SELECTED THERMOSETTING POLYMER SYSTEMS

RESIN FORMULATION	SAMPLE SIZE/ THICKNESS	DISTANCE (IN.)	EXPOSURE TIME	PULSE RATE PPS	OUTPUT (VOLTS)	LAMP POSITION	REMARKS
Atlac 382-051 ¹	10 gms/0.2"	3	40	8	2200	face down	no cure
Atlac 382-051)	10 gms/0.2"	3	50	8	2200	face down	surface hardened
Atlac 382-051)	10 gms/0.2"	3	60	8	2200	face down	hardened
Atlac 382-051)	10 gms/0.2"	3	120	8	2200	face down	hardened
Atlac 392-051)	10 gms/0.2"	3	150	8	2200	face down	mass cracked
Atlac 382-052)	10 gms/0.2	3	60	8	2200	face down	no cure
Atlac 382-052)	10 gms/0.2"	3	90	8	2200	face down	surface hardened
Atlac 382-052)	10 gms/0.2"	3	120	8	2200	face down	hardened
Atlac 382-052)	10 gms/0.2"	3	150	8	2200	face down	mass cracks
Atlac 382-052)	10 gms/0.2"	4	120	8	2200	face down	surface only
Atlac 382-052)	10 gms/0.2"	4	150	8	2200	face down	hardened
Atlac 387-13 ³) ⁴	10 gms/0.2"	3	150	8	2200	face down	hardened, cracks
Grace RCP 1072-72-2/3 ³)	9 gms/0.2"	4	60	8	2200	face down	hardened
Grace RCP 1072-72-2/31 ⁴)	9 gms/10.2"	4	30	8	2200	face down	hardened
Grace RCP 1072-72-2/31 ⁴)	10 gms/10.2"	4	15	8	2200	face down	no cure
Grace RCP 1072-72-2/31 ⁴)	10 gms/10.2"	4	30	8	2200	face down	hardened
Grace RCP 1072-72-2/31 ⁴)	10 gms/10.2"	4	15	8	2200	face down	no cure
Desolite 2237-111 ⁵)	10 gms/0.2"	4	60	8	2200	face down	no cure
Desolite 2237-111 ⁵)	10 gms/0.2"	4	120	8	2200	face down	hardened
Desolite 2237-111 ⁵)	10 gms/0.2"	4	150	8	2200	face down	cracks
Epocryl U12/TAC ⁶)	10 gms/0.2"	4	60	8	2200	face down	no cure
Epocryl U12/TAC ⁶)	10 gms/0.2"	4	90	8	2200	face down	hardened, tack
Epocryl U12/TAC ⁶)	10 gms/0.2"	4	120	8	2200	face down	hardened
Epocryl U12/TAC ⁶)	10 gms/0.2"	4	150	8	2200	face down	hardened
Araldite 6010/956 ⁷)	10 gms/0.2"	4	60	8	2200	face down	hardened
Araldite 6010/956 ⁷)	10 gms/0.2"	4	90	8	2200	face down	mass cracked

(Cont'd)

TABLE 7: FLASH POLYMERIZATION CURING RESULTS FOR SELECTED THERMOSETTING POLYMER SYSTEMS

RESIN FORMULATION	SAMPLE SIZE/ THICKNESS	DISTANCE (IN.)	EXPOSURE TIME	PULSE RATE PPS	OUTPUT (VOLTS)	LAMP POSITION	REMARKS
Ciba 0500/828/V40 ^{a)}	10 gms/0.2"	4	120	8	2200	face down	no cure
Ciba 0500/828/V40 ^{b)}	10 gms/0.2"	4	150	8	2200	face down	surface hardened
Ciba 0500/828/V40 ^{b)}	10 gms/0.2"	4	210	8	2200	face down	surface hardened
Ciba 0500/828/V40 ^{b)}	10 gms/0.2"	4	300	8	2200	face down	hardened
Ciba MY720/V40 ⁹⁾	10 gms/0.2"	4	210	8	2200	face down	mass cracked
Ciba MY720/V40 ⁹⁾	10 gms/0.2"	4	150	8	2200	face down	no cure
Ciba MY720/828/V40 ¹⁰⁾	10 gms/0.2"	4	180	8	2200	face down	hardened
Ciba MY720/828/V40 ¹⁰⁾	10 gms/0.2"	4	210	8	2200	face down	hardened
Ciba MY720/828/V40 ¹⁰⁾	10 gms/0.2"	4	240	8	2200	face down	mass cracked
Ciba MY720/828/V40 ¹⁰⁾	10 gms/0.2"	4	300	8	2200	face down	mass cracked

- 1 AtIac 382-05, 100 pts; RA70, 1 pt.
- 2 AtIac 382-05, 100 pts, USP 245, 1 pt
- 3 Grace RPC 1072-72-2/3; 50 pts each of 1072-72-2 and 1072-72-3
- 4 Grace RPC 1072-72-2/31; 50 pts of 1072-72-2 and 75 pts of 1072-72-3
- 5 Desolite 2237-111; 100 pts; RA70 1 pt.
- 6 Epocryl U12 70 pts; TAC 30 pts; BP 1 pt.
- 7 Araldite 6010 100 pt; H956 25 pts
- 8 Ciba 0500 60 pts, Epon 828 40 pts; 50 V40 pts
- 9 Ciba MY720 60 pts, Epon 828 40 pts; 40 V40 pts
- 10 Ciba MY720 70 pts, Epon 828 30 pts; 40 V40 pts

hypothesis that heat was an important if not the primary accelerator of this epoxy resin polymerization.

Several experiments were conducted which comprised the exposure of the resin filled aluminum dishes to the blast of a hot air gun (1000°F). The results obtained were qualitatively quite similar to those obtained via flash polymerization. The suggestion that heat exposure is instrumental in the promotion of this polymerization would therefore appear to have considerable validity.

Additional experiments were carried out on the flash polymerization of various other thermosetting polymer systems with emphasis on unsaturated polymers which were deemed by Xenon Corporation to be prime candidates for their process. All the unsaturated polymer samples (Atlac, Grace, Desolite, Epocryl) contained a peroxide catalyst or equivalent. When this catalyst was omitted, cure times were unsatisfactorily long. These resin samples were exposed to flash polymerization in aluminum dishes similarly to the above described epoxy resin experiments. The results of these exploratory studies are summarized in Table 7.

The results of these and other flash polymerization experiments were deemed inconclusive. Significant reductions in cure times were obtained with both unsaturated thermosetting resins (Atlac, Grace, Desolite, Epocryl) and also epoxy polymer systems. The main cure mechanism seems however, to be thermally initiated from the energy input of the pulsed xenon lamps. It is interesting to note moreover, that the unsaturated thermosetting resins required the presence of a conventional catalyst to obtain the short cure periods. As discussed in the previous chapter of this report, the presence of such catalysts is not needed with electron beam radiation curing. The high cure speed of the epoxy resin systems which were evaluated can be at least partially explained by a high exotherm activated by a rapid rise in the temperature of the polymer samples. Data are available in the technical literature

which show that epoxy resin systems can be cured quite rapidly at suitably elevated temperatures.

Additional experimentation is recommended in order to obtain an adequate evaluation of the merits of flash polymerization as a room temperature curing technique. This applies to both equipment particularly as regards available curing areas (which are very limited for most practical applications) and also materials. It would appear that at the present state of development flash polymerization applications may be limited to rather special situations where certain concrete advantages can be realized from this polymerization technique.

VI. INTERFACIAL POLYMERIZATION

Interfacial polymerization in various forms has been extensively investigated for over two decades with primary emphasis directed towards the preparation of synthetic fibers. As used in the context of these studies, however, the term designates a process where a storage stable polymerizable composition without polymerization catalysts or the equivalents thereof comprises one phase and is made to contact another phase containing the catalyst, said contact resulting in initiation of the polymerization at the interface. Such reactions are known and can be initiated and carried through at ambient temperatures. Potential applications range from curing fiber reinforced composites to structural adhesive compositions.

Two embodiments of this polymerization approach for applications of interest in this research are 'prepromoted' glass fiber mat reinforcements developed by the Ferro Corporation about ten years ago^{20) to 23)} and more recently, the advent of the so called "second generation" structural acrylic adhesives.^{24), 25)} The 'prepromoted' glass fiber mat reinforcements consisted of glass fiber mats treated with a promoter system capable of causing the room temperature polymerization of unsaturated polyester type resins by initiating the free radical curing reaction.²⁶⁾ When these glass mat reinforcements were "wet out" with a high temperature peroxide precatalyzed polyester resin, polymerization commenced at room temperature with gel formation followed by curing of the polyester resin impregnated glass fiber mats. 'Prepromoted' fillers can be used as well as fiber reinforcements for this process.

More recently interfacial polymerization techniques are being applied to effecting room temperature cures of certain structural adhesives.²⁴⁾ A number of firms have introduced interfacially curing adhesive compositions which polymerize at ambient temperatures to form strong and durable

bonds between a great many different substrates.²⁵⁾ One such adhesive system comprises a 100% reactive acrylic graft copolymer dissolved in a blend of acrylic monomers plus an activator system. The graft copolymers contain certain modifying moieties which not only reinforce and toughen the bonds, but also provide additional active chemical sites which promote the polymerization reaction. Adhesion takes place at ambient temperatures when the monomers and the activator graft polymerize in the glue line.

The more important material and polymerization characteristics for a both technically effective and economically viable ambient temperature interfacial polymerization process include the following:

A. 'Prepromoted' Reinforcements or Fillers

'Prepromoted' reinforcements or fillers must have long term chemical and physical stability to a range of temperatures, humidities, etc. with no loss of effectiveness. The prepromoted materials should likewise be non-flammable, non-toxic, readily handled by conventional procedures and storage stable at the usual temperatures and other environmental conditions.

B. Resin System

The resin system must likewise feature long term chemical and physical stability to a range of temperatures, humidities, etc., without loss of pertinent properties particularly as regards curing characteristics. Other desirable features include non-toxicity, non-flammability, ease of handling by conventional procedures (viscosity, wet-out) and prolonged storage capability at the usual temperature and other environmental conditions.

C. Polymerization

Controlled and reproducible gel and cure times are of course, a prime requirements. Additional desiderata are non-tacky surfaces with

air cures, completeness of polymerization at ambient temperatures as evidenced by the usual chemical and physical tests and achievement of cure with contact pressures only.

If these material and processing characteristics can be successfully attained, interfacial polymerization is proposed as offering the following significant benefits compared to the conventional polymerization techniques which are presently employed for room temperature curing:

- 1) no mixing of catalysts, promoters, etc., with the resin system is required, hence no chance for mixing errors
- 2) no calculations of catalyst, promoter amounts and ratios with resins are needed, hence no possibility of mistakes
- 3) no weighing or metering flammable and/or toxic materials
- 4) controllable and reproducible gel times
- 5) rapid cure over a wide temperature range even in the presence of moisture
- 6) no skilled labor needed to produce high quality products
- 7) ultimate simplicity in factory or field processing and repair
- 8) energy efficient -- no external heat source needed for curing.

Interfacially curing polymer systems could be supplied as two-component kits ready for use. For the production of fiber reinforced laminates for example, such a kit would contain as one component the prepromoted fiber reinforcement in any convenient form such as rolls of some specified width, etc. The other component would be the precatalyzed resin composition. Processing would essentially comprise merely cutting shapes of the desired dimensions of the prepromoted reinforcement from the roll and then wetting them out. An adhesive or sealant kit would be composed

similarly of an activator and a resin component. Adhesion would be achieved by applying first the activator on the surfaces to be bonded or sealed followed by later application of the resin component and the assembly of the parts when needed.

Exploratory experiments were carried out on both of the above described embodiments of the interfacial polymerization approach. Liquid thermosetting resins with unsaturated groups (double bonds) were selected for the initial experimental studies. The specific resins investigated were styrenated polyesters and acrylic resin syrups, vinyl esters, polybutadienes, urethane acrylics and also variously modified polyimides. Later experiments were carried out with epoxy resins and other non-free radical types of the thermosetting resins. These resins were used as matrices for the preparation of fiber reinforced composites at room temperatures using 'prepromoted' fiber reinforcements. Some experimental work was also carried out on the formulation and cure of adhesive, sealant and casting compositions, also at ambient temperatures.

Prepromoted reinforcements were prepared for wet out with vinyl and/or allyl types of unsaturated resins by treatment of reinforcing fibers such as glass and Kevlar cloth (style 181 or equivalent) with an organic peroxide solution in a volatile organic solvent. The peroxide selected was benzoyl peroxide, an initiator well known for its capability to polymerize the above noted unsaturated polymers. The organic solvent used in the initial experiments was acetone. Later experiments employed halogenated solvents. Upon the evaporation of the solvent, peroxide treated 'prepromoted' fiber reinforcements were obtained.

Boron trifluoride complexes and aliphatic amines were deposited on glass and Kevlar fiber cloth reinforcements from organic solvent solutions in order to obtain prepromoted fiber reinforcements for the interfacial polymerization of epoxy resins at ambient temperatures. Shell Chemical Company's 828 resin

was employed for impregnating the prepromoted glass fiber cloths. Various proprietary curing agents were used in conjunction with furfural alcohol, resorcinol and other types of thermosetting resins for prepromotion of fiber reinforcements. All of these experiments gave unsatisfactory results in that the desired polymerization reaction could not be effected.

Selected free radical types of polymerizing thermosetting resin compositions formulated for room temperature curing with an amine accelerator were employed to wet out and impregnate the prepromoted fiber reinforcements comprising either glass or Kevlar 181 style cloth. Laminates up to approximately 0.150" thick were then prepared (using up to 15 plies of thusly 'prepromoted' cloth reinforcements) at room temperature via interfacial polymerization, i.e., contacting the prepromoted reinforcing fibers with the various matrix resins. Contact pressures only were employed for the preparation of these laminates. Prepromoted inorganic fillers were incorporated into similarly formulated resin compositions for possible adhesive, sealant and coating applications.

Non-free radical types of polymerizing thermosetting resin compositions were treated in the same manner with emphasis on epoxy resins. However, as noted above contacting such resins with variously 'prepromoted' reinforcing fibers did not produce the initiation of the polymerization reaction at ambient temperatures or even at elevated temperatures. At present the concept of effecting room temperature cures with prepromoted reinforcements seems to be applicable only to thermosetting resin compositions which polymerize by a free radical type of cure mechanism. No data could therefore be obtained with these other resin systems.

Approximately 140 laminates were prepared by the interfacial polymerization technique with peroxide prepromoted glass and Kevlar cloth reinforcements and various free radical curing resins. Some experiments were also carried out with cotton fabric reinforcements. All the laminates were made with the application of contact pressure only at ambient temperature conditions.

Specific matrix resins which were used to impregnate these prepromoted fiber reinforcements, included the following:

- 1) styrenated polyester resin syrups: Koppers V7000; Atlac 382/styrene (70/30 wt ratio); Atlac 382/diethyleneglycoldimethacrylate (70/30 wt ratio); Atlac 382/trimethylolpropanetrimethacrylate (70/30 and 60/40 wt ratio).
- 2) acrylic modified urethanes: Thiokol Uvithane 783/styrene (60/40 wt ratio); Thiokol Uvithane 783/diethyleneglycoldimethacrylate (30/70 wt ratio); Nisso TE2000/diethyleneglycoldimethacrylate (50/50 wt ratio).
- 3) Triallylcyanurate modified polyester resin syrups: Atlac 382/triallylallylcyanurate(70/30 wt ratio); Atlac 382/triallylisocyanurate (70/30 wt ratio)
- 4) Vinyl esters: DOW XD7156
- 5) 1, 2 polybutadiene and copolymers: Ricon 100, 150 and 157
- 6) proprietary modified acrylic resin compositions: Versiloks 506, 510 and 516 (with Accelerator #4).

The most promising results were obtained with benzoyl peroxide catalyst or Accelerator #4 'prepromoted' glass fiber and Kevlar cloths after impregnation with either the DOW XD7156 or the Versilok 516 resin. Accelerator #4, a proprietary product supplied by Hughson Chemical Co. who also produce the Versilok resins, is understood to be also an organic peroxide type of material. The Versilok resins were used as supplied without any added room temperature polymerization promoter. All the other resin systems were compounded with varying amounts of dimethyltoluidine as a room temperature promoter (0.1% - 3% on a wt basis).

Table #1 summarizes some representative physical strength properties of laminates prepared from such prepromoted fiber reinforcements and various free radical curing thermosetting resin compositions. As noted above, all cures were carried out at ambient temperatures and contact pressure only. Strength

properties are seen to be fairly representative of room temperature cured laminates with similar amounts of fiber reinforcements. Gel times of these systems were in the order of less than 5 to 40 minutes. Using strength properties and Barcol hardness as criteria, full cure was considered achieved after about 6 hours.

The gel times obtained in the experiments described in Table 1 were rather short and would tend to limit practical applications for this interfacial curing technique. Additional experiments were therefore carried out to ascertain if gel times could be changed to meet the varying use requirements. It was found that gel times could be widely and reproducibly altered by changing the amount of the inhibitor present in these free radical curing types of resin matrixes. Hydroquinone, a very widely used free radical polymerization inhibitor, was employed for this purpose. Table 9 shows the effect of inhibitor changes on both gel and cure times of Dow resin XD 7156. The physical strength properties of laminates made by impregnating prepromoted fiber reinforcements with resin matrixes containing different amounts of hydroquinone inhibitor were also determined. Strength properties were found to be independent of resin matrix inhibitor level provided additional time was allowed for curing.

Exploratory experiments were conducted with castings of Dow XD 7156 resin containing peroxide prepromoted 3M glass microspheres as fillers (approx. 30 wt%). The prepromotion of the glass microspheres was accomplished in the same manner as that of the fiber reinforcements discussed above. The results obtained were encouraging in that cure at ambient temperatures was obtained as desired. Similar results were realized when Versilok resin 516 or Koppers V7000 resin were employed in place of the Dox SC7156 resin. The castings measured approximately 2" diameter and were about 3/16" high.

TABLE 8: SOME REPRESENTATIVE PHYSICAL STRENGTH PROPERTIES OF CLOTH REINFORCED LAMINATES PREPARED WITH PEROXIDE PREPROMOTED FIBER REINFORCEMENTS CURED AT AMBIENT TEMPERATURES AND CONTACT PRESSURES

LAMINATE COMPOSITIONS	REINFORCEMENT PREPARATION	WEIGHT & FIBER REINFORCEMENT	FLEXURAL STRENGTH PSI	FLEXURAL MODULUS PSI X 10 ⁶	COMPRESSIVE STRENGTH	COMPRESSIVE MODULUS PSI X 10 ⁶
Versiloks 516; 181 glass cloth, CS316 finish 12 plies, 0.132" thick	Accelerator #4	34	24,600	0.8	31,200	1.05
Versiloks 516; 181 glass cloth, CS316 finish, 12 plies, 0.135" thick	Benzoyl peroxide	45	45,800	1.4	42,600	1.16
Versilok 516; 181 glass cloth, CS316 finish, 12 plies, 0.132" thick	Accelerator #4	47	43,600	1.4	41,800	1.15
Dow XD7156 ⁽²⁾ -Kevlar Style 348 cloth, CS800 finish 12 plies, 0.153" thick	Accelerator #4	32	25,200	1.3	21,400	0.82
Dow XD7156 ⁽²⁾ -Kevlar Style 348 cloth, CS800 finish, 12 plies, 0.148" thick	Benzoyl peroxide	36	28,100	1.4	22,300	0.75
Dow XD7156 ⁽²⁾ -Kevlar Style 348 cloth, CS800 finish, 12 plies, 0.142" thick	Benzoyl peroxide	43	34,000	1.3	28,400	0.82
Dow XD7156 ⁽²⁾ - 181 glass cloth, CS316 finish; 12 plies; 0.140" thick	Benzoyl peroxide	41	27,300	1.2	30,600	0.92
Dow XD7156 ⁽²⁾ -181 glass cloth, CS316 thick; 12 plies, 0.130" thick	Accelerator #4	46	45,300	1.5	33,700	1.10

- 1) approximately 2 wt% peroxide or Accelerator #4 based on weight of cloth reinforcements
- 2) as supplied by the manufacturer resin has 80 ppm inhibitor content; 0.75% dimethyltuidine added as room temperature

TABLE 9: GEL AND CURE TIMES VERSUS HYDROQUINONE INHIBITOR CONTENT FOR DOWN RESIN XD7156*

HYDROQUINONE CONTENT, PPM	GEL TIME MINUTES	CURE TIME, HOURS BARCOL HARDNESS 60
800	35	~ 12 hours
500	25	~ 8 hours
375	15	~ 8 hours
250	10	< 6 hours
100	< 8	< 4 hours
80	< 5	< 4 hours

* As supplied by manufacturer, resin has 80 ppm inhibitor content

The Versilok 516 Accelerator #4 system was investigated for adhesive applications which are the recommended use for this material combination. 6"x1"x1/8" 2024 aluminum lap shear test specimens (1" overlap) were used for this purpose. Accelerator #4 was coated onto one of the aluminum surfaces and the volatile organic solvent permitted to evaporate. The Versilok 516 resin was then applied on the other aluminum surface and the lap shear specimen assembled using strapping tape to hold it together. Tensile shear strengths were measured to be in excess of 2500 psi after a 6 hour cure at ambient temperature. Increasing the cure time to 12 hours and then to 24 hours respectively, did not produce significant tensile lap shear strength improvements. Similarly promising results were obtained on FRP and also steel surfaces.

Adhesive compositions were prepared in the same manner with the Dow XD7156/benzoyl peroxide system. The lap shear strengths obtained with 2024 aluminum specimens (1" x 6" x 1/8", 1" overlap) were somewhat lower. They measured between 1600 to 1800 psi. Again increasing the cure time to 12 hours and 24 hours respectively did not improve the tensile lap shear strength. Adhesion to other surfaces such as FRP and steel, was also somewhat lower than for the Versilok 516/Accelerator #4 system.

The limited experimental studies indicate that interfacial polymerization techniques offer definite promise for simplified ambient temperature curing of laminates, adhesives, sealants and casting compounds. At the present however, the technique appears to be definitely limited to free radical types of thermosetting resin systems. The major potential advantage of this room temperature polymerization method is that it eliminates problems associated with metering, weighing and mixing. The most important problem is the realization of 'prepromoted' reinforcements which have long term stability to various temperatures, humidities and other environmental conditions that

may be encountered during storage. The solution of this problem lies in the development and formulation of promoters with enhanced long term thermal and chemical stability for deposition on fiber reinforcements, fillers, etc. Additional studies to extend our understanding and to develop specific applications for this room temperature curing technique are recommended.

VII. ANAEROBIC CURING

Anaerobic polymers have achieved widespread usage for adhesives and sealants due to their unique cure mechanism which takes place at ambient temperatures only when they are enclosed between active surfaces such as metal parts, in the absence of air.²⁸⁾ These polymers are furnished as one component system which makes them convenient to use and have the capability to be chemically and physically modified and formulated to fit a wide variety of applications and use conditions. At present their major use ranges from thread locking adhesives and sealants to bonding various metal parts at room temperature conditions.

Recent developments in the technology of anaerobically curing polymers have greatly enhanced their physical and chemical properties and raise questions regarding their possible use for applications other than room temperature curing adhesives and sealants. The concept of employing one component polymer compositions which can be cured at ambient temperatures by the removal of air only, is certainly an attractive one for the manufacture of a great many nonmetallic components including fiber reinforced laminates, potting compounds, etc. A limited number of experiments were therefore carried out to ascertain the potential of anaerobic curing techniques for curing the various nonmetallic parts of interest to the Naval Air Systems Command.

²⁸⁾
Anaerobic cure systems are based on a free radical cure mechanism. Free radicals generated by metal contact or other means, react readily with the monomer molecules to cure them into hard, tough cross-linked thermoset types of plastics at ambient temperatures. The 100% reactive anaerobic monomers are converted into these thermoset plastics with minimal shrinkage during cure. The cured products have thus proved very effective for bonding various parts together and sealing assemblies against leakage and also internal corrosion.

The traditional or 'first generation' anaerobics were basically polymerized di-or trimethacrylate esters and used for thread locking metallic bolts and screws, sealing flanges and bonding smooth cylindrical parts. Modification of the monomer molecules with specific functional groups and/or other monomers such as for example, urethanes extends their usage to a wide variety of high performance adhesive/sealant applications while maintaining such desirable characteristics as fast room temperature cures with minimal shrinkage. Also accelerators or primers are now available for bonding to nonmetallic surfaces again in the absence of air only.

Recently urethane modified dimethacrylate polymers have been developed which can be readily and quickly cured anaerobically at ambient temperature.²⁸⁾ This exhibit the superior adhesive strength and toughness typical of the urethane family of polymers plus the 'ease of cure' characteristics of the conventional one component anaerobic polymer compositions. These new polymeric materials are reported to bond well and furnish excellent seals not only to metallic surfaces but also to various thermosetting plastics, glasses and ceramics. Tensile strengths in excess of 6000 psi and impact strengths as high as 500 ft/lb air have been claimed for these improved anaerobic adhesives and sealants.

Still later developments relate to technical advances which substantially upgrade the thermal stability of anaerobically cured polymer systems.²⁹⁾ Anaerobically cured resins have become available which offer high physical strengths and long term durability at temperatures as high as 450°F.³¹⁾ Recently introduced anaerobic heat resistance adhesives feature a 3000 psi lap shear tensile strength (iron/iron) after cure at room temperature at only contact pressures. As much as 75% of the original lap shear tensile strength is said to be retained after 2500 hours of 450°F exposure in air. These heat resistant anaerobically curing polymers are understood to be acrylic modified polyimides. Extension of anaerobic cure technology to polyimides is of very real interest for the

aerospace field with its many high temperature adhesive and sealant applications.

Anaerobically curing polymers are thus obviously candidates for exploratory studies of high molecular weight materials which can be cured at ambient temperatures. Obvious advantageous characteristics of these 100% reactive products include absence of solvents; no need for mixing; no noxious or volatile products given off during cure; good physical strengths chemical and thermal stability, etc. Potential application areas of adhesives and sealants for both metallic and nonmetallic substrates, composites and potting compounds.

Lap shear strength experiments were first carried out on anaerobic cures at room temperature of various commercially available adhesive compositions made by the Loctite Corporation of Newington, Conn. The specific adhesives investigated were Loctite 306, 312, 317 and L0-559. Table #10 summarizes the properties of these materials in the uncured (liquid) state.²⁹⁾ Strips of 2024 aluminum alloy (1" x 6" x 1/8") were prepared for bonding with these adhesives by the standard FPL acid dichromate etching procedure.

To assemble the specimens, a few drops of the adhesive composition were distributed on a one-inch square area of one aluminum strip and the second aluminum strip was positioned above the first so as to produce a one-inch square lap joint. The metal surfaces were pretreated with Loctite Accelerator #707 before placement of the adhesive. The assemblies were then tightly wrapped with glass fiber reinforced strapping tape to maintain their configuration during handling and curing. Bond lines were in the order of 5 mils or less. Single lap shear strengths were measured at ambient temperatures and after 500 hours of aging in air at 350°F; water, JP 4 and acetone immersions at room temperature.

The results of these experiments are summarized in Table #11. The data show that all four Loctite adhesives had tensile lap shear strengths in the

TABLE 10: PROPERTIES OF SELECTED MODIFIED THERMOSETTING ACRYLIC ADHESIVES IN THE UNCURED (LIQUID) STATE

ADHESIVE DESIGNATION	LOCTITE 306	LOCTITE 312	LOCTITE 317	LOCTITE LDS-L0-559
Base	modified acrylic	modified acrylic	modified acrylic	modified acrylic
Color	clear amber	clear amber	clear amber	light yellow
Specific gravity	1.1	1.1	1.1	1.1
Viscosity, CPS	10,000 min	1000 min	3000 min	70,000 - 120,000
Toxicity (primary eye irritant)	low	low	low	low
Flash point (TCC)	> 200°F	> 200°F	> 200°F	> 200°F
Shelf life ¹⁾	1 yr min	1 yr min	1 yr min	3 mos min
Operating temperature range	-65 to 400°F	-65 to 200°F	-65 to 300°F	-65 to 450°F

1) Shelf life in 100 cc containers is 1 year minimum, shelf life in liter containers is three months minimum except for LDS-L0-559 whose shelf life is less as indicated above.

order of 2000 psi after a 24 hour cure at room temperature. It should be noted that contact pressure only was applied during the curing process. After 500 hours of exposure to air at 350^oF, the tensile lap shear strengths of Loctite adhesives 306, 312 and LDS-LO-559 held up very well. As a matter of fact the tensile lap shear strength of adhesive LO-559 showed a significant increase of close to 20%. The tensile strength of Loctite adhesive 317 showed a definite drop after this 500 hour-350 F exposure test. Also 500 hours immersion in water, JP-4 and acetone at room temperature did not affect the tensile lap shear strengths disadvantageously with the exception of Loctite adhesive 312 which apparently lacked acetone resistance.

Additional lap shear strength tests were carried out with Loctite adhesive LO-559 which is reported to offer the greatest thermal stability of the entire Loctite adhesive line. These tests which were carried out in the same manner as those described previously, are shown in Table #12. Information on a similar adhesive compounded at New York University is included in the table. The test data show significant tensile lap shear strength retentions after prolonged air exposures to temperatures as high as 450^oF. These results are promising particularly in view of the very simple bonding procedure used especially when compared to the complexities of current structural bonding technology.

A considerable amount of work was carried out to extend the range of anaerobic technology to curing fiber reinforced laminates and castings at room temperature. The general approach was to remove air from a layup or casting by means of a high vacuum pump in order to obtain anaerobic conditions. The results were disappointing in that no cure was obtained unless the section thickness of the polymer was in the order of about 20 mils or less. These and other experiments suggest that the anaerobic cure mechanism may well be dominated by the diffusion of catalytic metal ions from the metal surfaces into the resin. It seems to be quite a short range phenomenon in that while the resin layers close to the metal surface cure, the "interior" of the resin remains liquid.

TABLE 11: SINGLE LAP SHEAR STRENGTH PROPERTIES OF SELECTED ANAEROBICALLY CURED ADHESIVES
SINGLE-LAP SHEAR STRENGTH (PSI)*

ADHESIVE	INITIAL**	500 HOURS AGING IN MEDIUM			
		AIR at 350°F	WATER AT RT	JP4 at RT	ACETONE at RT
Loctite 306	1890	1760	1880	1810	1905
Loctite 312	2050	2150	2040	1940	365
Loctite 317	2180	1590	1920	2130	2120
Loctite LDS-L0-559	1830	2260	2160	2090	1730

* adherents 2024 aluminum alloy

** cure time 24 hours at room temperature

TABLE 12: SINGLE LAP SHEAR STRENGTH PROPERTIES OF ANAEROBICALLY CURED LOCTITE ADHESIVE LO-559
AFTER HEAT AGING AT 450°F

TENSILE LAP SHEAR, PSI	HEAT AGING AT 450°F IN AIR			
	1 WEEK	3 WEEKS	6 WEEKS	12 WEEKS
aluminum/aluminum, 2024 alloy, LO-559	2160	2240	1730	1650
steel/steel, sandblasted*	2350	2300	1800	1750
aluminum/aluminum, 2024 alloy, NYU adhesive**	2060	2130	1920	1560

* Loctite Company Data, bulletin LDS-LO-559

** NYU Formulation: Rhone Poulenc Kerimid 601/ethyleneglycol dimethacrylate
60/40 wt ratio with 50 pts

Anaerobic room temperature cures offer many attractive features including employment of a ready to use one component adhesive without mixing, pot life problems, etc. The presently developed polymer compositions are however, limited in applicability to adhesives and sealants due to the nature of the cure mechanism. Additional R & D is suggested in order to optimize the potential of anaerobic room temperature cures, for structural bonding and sealant applications.

VIII. AMBIENT TEMPERATURE CURING POLYMER COMPOSITIONS WITH HIGH TEMPERATURE SERVICE CAPABILITIES

Ambient temperature polymer compositions with high temperature service capabilities are of obvious interest for the preparation of fiber reinforced composites, adhesives, sealants, potting compounds, etc. Experimental studies were briefly conducted to explore the development of such compositions and to evaluate them at both ambient and elevated temperature conditions. Because of their exceptionally desirable balance of physical and chemical properties, unique compounding versatility and ready processing characteristics, epoxy resins were selected for exploratory work. The experiments were limited to adhesives and fiber reinforced composite structures.

Epoxy resin compositions which cure at room temperature and have high temperature service capability have long been of considerable interest especially for repair of nonmetallic structural components. The present state-of-the-art is represented by Aerospace Adhesive EA 934 (Hysol Dexter Corp.) and Armstrong A-66 Epoxy Adhesive (Armstrong Products Company). These proprietary adhesive compositions cure at ambient temperatures and have significant lap shear strengths (aluminum/aluminum) even after exposures to temperatures as high as 400⁰F for more than 200 hours. Data on an alternative epoxy resin composition which features a low temperature cure and high temperature service properties have recently been published by researchers of the Hughson Chemical Co. (Erie, Pa.). The Hughson system is said to be applicable for the preparation of both adhesives and fiber reinforced laminates.

The exploratory epoxy formulation investigated at New York University comprised specific two component systems which when mixed together cure at ambient temperature with hopefully high temperature service properties. Component "A" was a blend of a multifunctional epoxy resin with a conventional epichlorohydrin bisphenol A resin (epoxy equivalent weight 180-195). A number of different blends of these two components were investigated. Two such

blends considered to be promising on the basis of quantitative evaluations were Ciba Geigy Resins 0500/6010 (70/30 wt ratio) and Ciba Geigy MY720/6010 (70/30 wt ratio). Ciba Geigy Resins 0500 and MY720 are tri and tetrafunctional respectively and 6010 is a typical epichlorhydrin bisphenol resin (EEWt 180-195). The epoxy component "B" was based on a long chain polyamide such as General Mills Chemical Company's Versamid 140 or Jefferson Chemical Company's Jeffamines D-230, D-400 and D-2000. Some experimental work was also carried out with Ciba Geigy proprietary hardener 956 for use as component "B".

Figures 9 to 12 summarize the effects of heat aging in air at 200°C on tensile strength characteristics of glass reinforced laminates prepared with such room temperature curing epoxy compositions. The test data show compositions, containing hardener 956 have substantially better tensile strength retentions upon 21 days exposure to 200°C than those prepared with the Versamid 140 and the Jeffamine blend. The tensile strength of the glass cloth laminate prepared with the 956 hardener was still around 30,000 psi after the 21 day exposure to 200°C.

A few experiments were also carried out with room temperature curing epoxy adhesive compositions of the same types. Lap shear strength data were obtained for aluminum/aluminum specimens (1 square inch overlap) at both ambient and elevated temperatures. The room temperature lap shear strengths after a 24 hour room temperature cure typically ranged from 2100 - 2300 psi. Lap shear strengths after 48 hours exposure at 220°C fell to around 1400 psi. The lap shear strengths after 96 hours exposure at 200°C and tested at room temperature, were in the 1700 psi range.

These few results are considered encouraging as they show that room temperature curing epoxy compositions can be formulated from rather simple and readily available resins and curing agents which exhibit quite respectable strength retentions even after prolonged exposures to temperatures as high as 200 C. It is proposed that the elevated temperature performance of such

room temperature curing epoxy compositions could be substantially enhanced by developing more sophisticated curing agents which include curing components with high temperature service capabilities. Such materials are known in epoxy technology. Successful development of such room temperature curing epoxy resin composition with high temperature performance seems quite feasible technically and when accomplished will fill a definite void in our present epoxy formulary, especially for field repair of aerospace components and the like. Furthermore, the concepts developed in such a study could with appropriate modifications be applicable to other thermosetting resin systems.

IX. SUMMARY

The performance properties of thermosetting polymer systems which are cured with the application of heat and pressure generally surpass those obtained with ambient temperature cures for the same systems. This report describes a program of research and development comprising the exploration and study of selected novel ambient temperature curing techniques with the goal of obtaining performance characteristics which will equal or surpass those achieved with conventional heat/pressure type cures.

The specific new room temperature curing methods experimentally investigated included electron beam radiation, flash polymerization, interfacial polymerization and anaerobic cures. Some experiments were also carried out on the development of room temperature curing polymer systems with high temperature service capabilities. All these novel curing techniques have advantages and limitations. The major advantages relate to the formulation of easy-to-use one component systems free from mixing and pot life limitations and rapid cures. At present these systems are however, limited to polymer compositions which cure by a free radical mechanism. Potential uses of these room temperature cure systems include fiber reinforced laminates, adhesives, sealants and potting compounds.

Electron beam radiation curing appears to be a cost effective method for line of sight curing free radical type thermosetting polymer systems at high speed and at ambient temperature. To justify the large equipment investment required for an electron beam accelerator, a volume production requirement should exist. Flash polymerization with pulsed xenon lamps requires additional technical development both as regards equipment and materials. It may be applicable at this time for curing continuous profiles such as small diameter pipe.

Interfacial polymerization with prepromoted fiber reinforcements or prepromoted fillers offers a number of advantages with negligible equipment

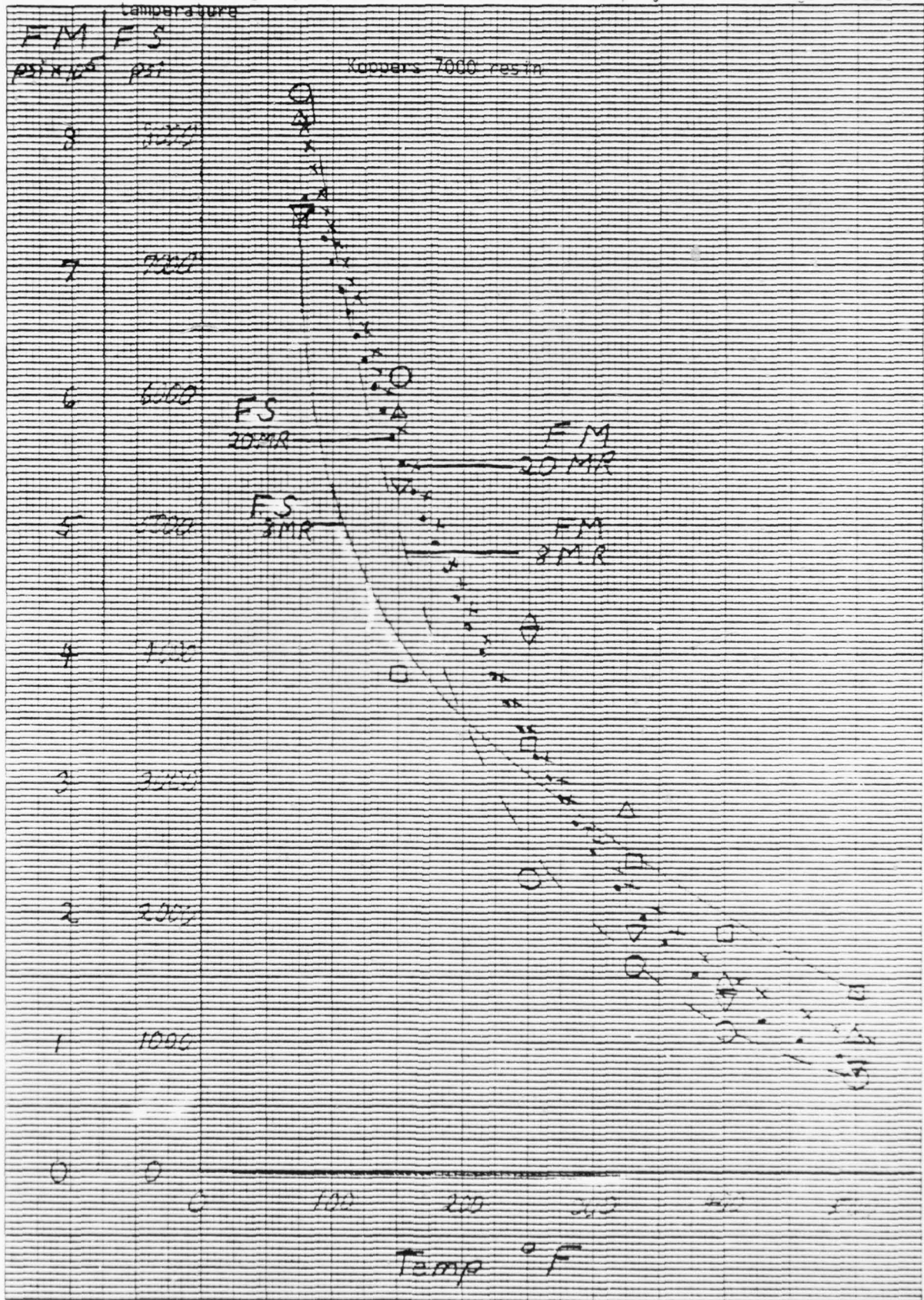
investment. The process requires however, further development especially for an industrially acceptable system capable of long term storage with no loss of effectiveness. Anaerobic cures are apparently limited to adhesives and sealant applications with the presently available polymer compositions. A very real immediate potential is soon in structural adhesive bonding especially with metal surfaces. The development of room temperature curing polymer systems with high temperature service capabilities is viewed as a promising and attainable goal particularly with epoxy type resin systems.

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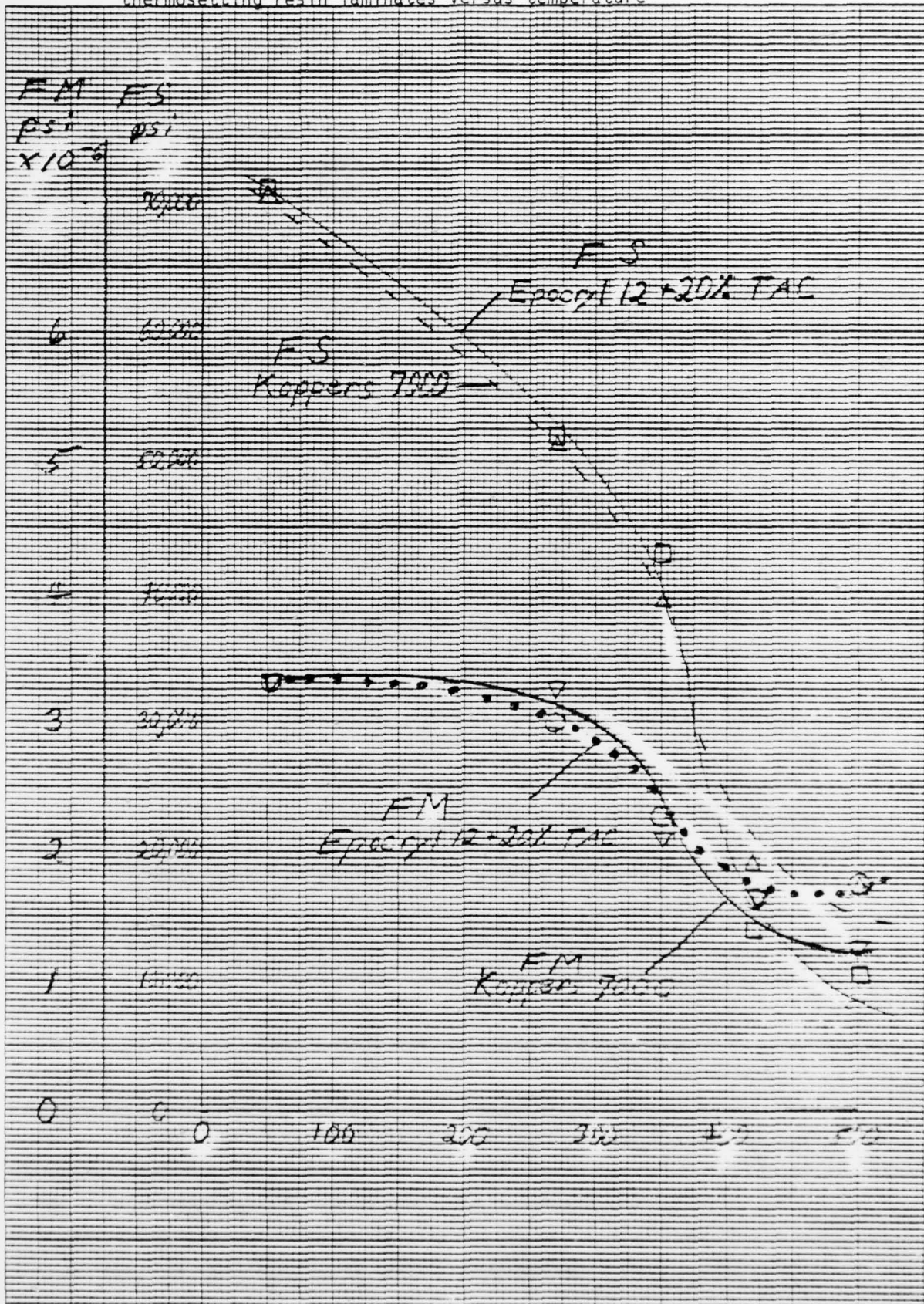
Fig. 1 Physical strength properties of radiation cured polyester castings versus



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K-E 10 X 10 TO 1/2 INCH 7 X 10 INCHES
NEUFEL & ESSER CO. MADE IN U.S.A.

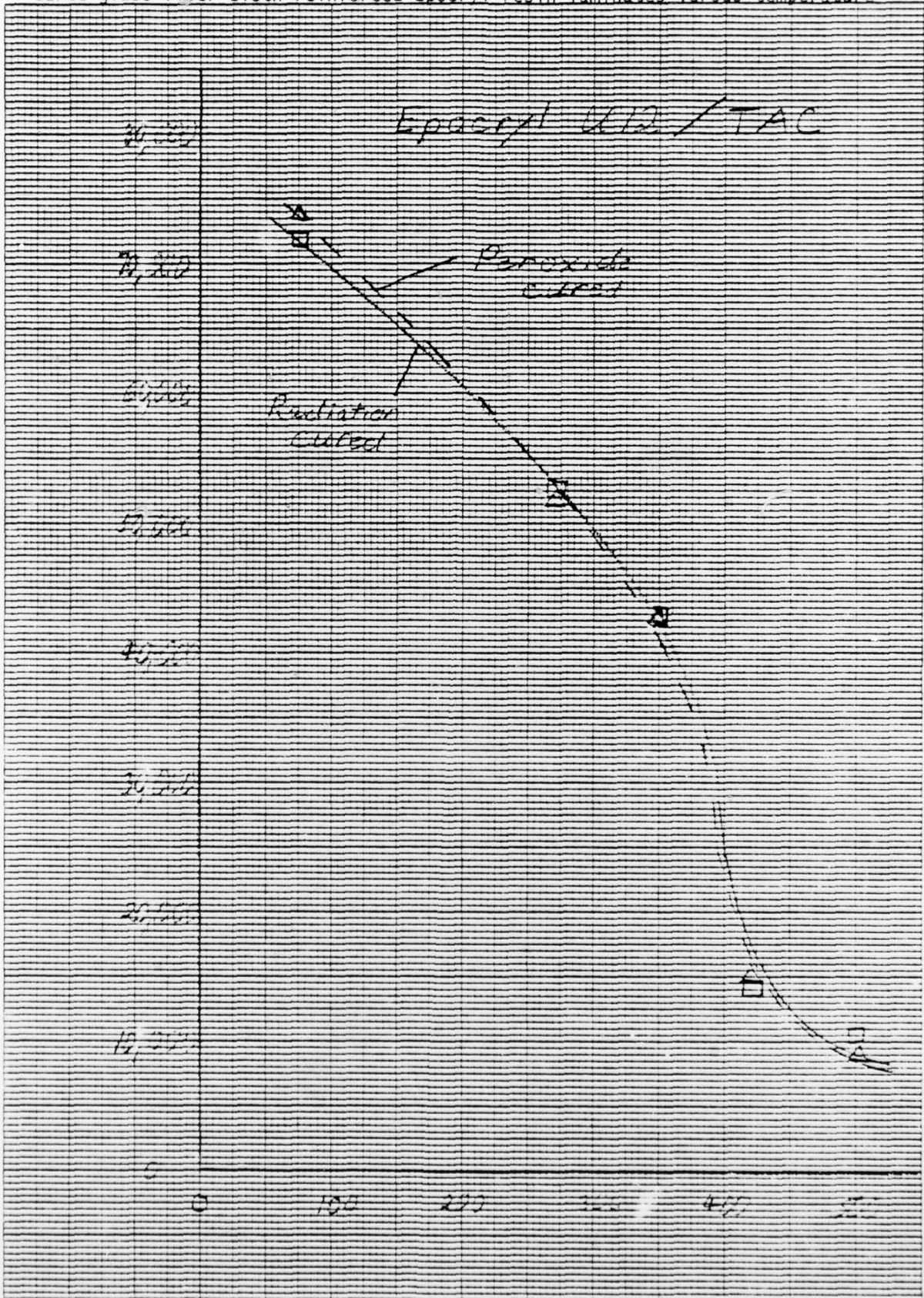
Fig. 2 Physical strength properties of radiation cured glass fiber cloth reinforced thermosetting resin laminates versus temperature



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Fig. 3 Comparison of physical strength properties of radiation versus peroxide cured glass fiber cloth reinforced Epocryl resin laminates versus temperature



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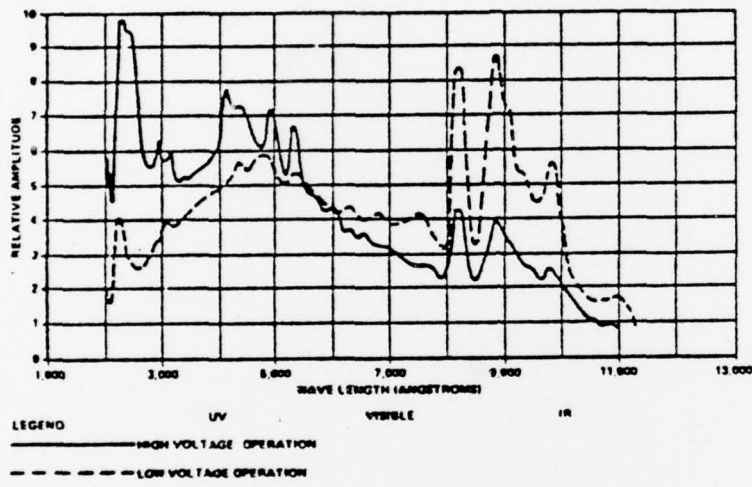


FIGURE 4. SPECTRAL DEPENDENCE ON ELECTRICAL OPERATING PARAMETERS

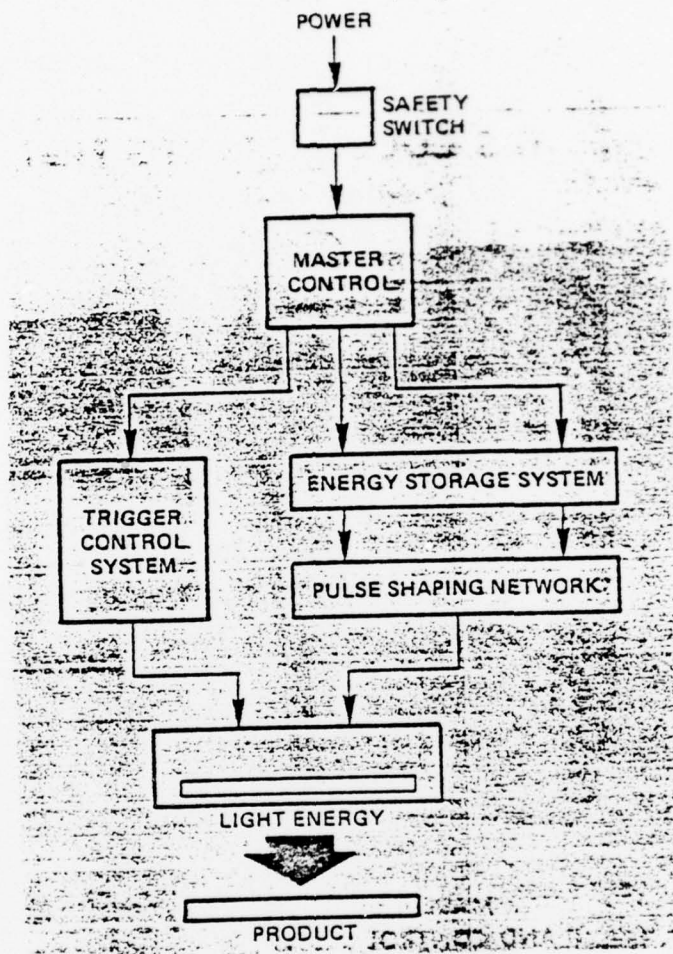
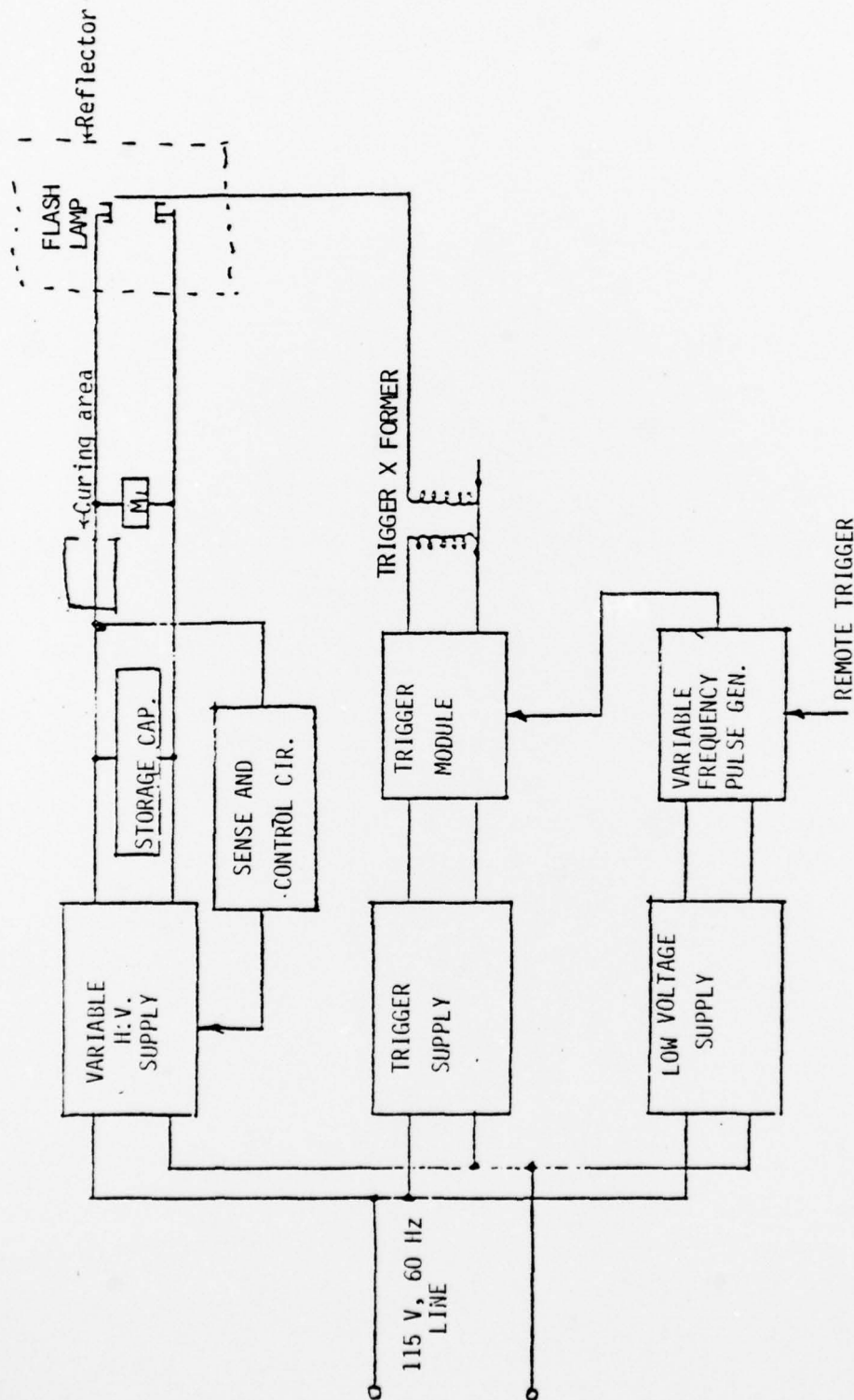


FIGURE 5: Energy conversion for Model 564 Xenon flash polymerization laboratory unit

FIGURE 6. BLOCK DIAGRAM XENON MODEL 564

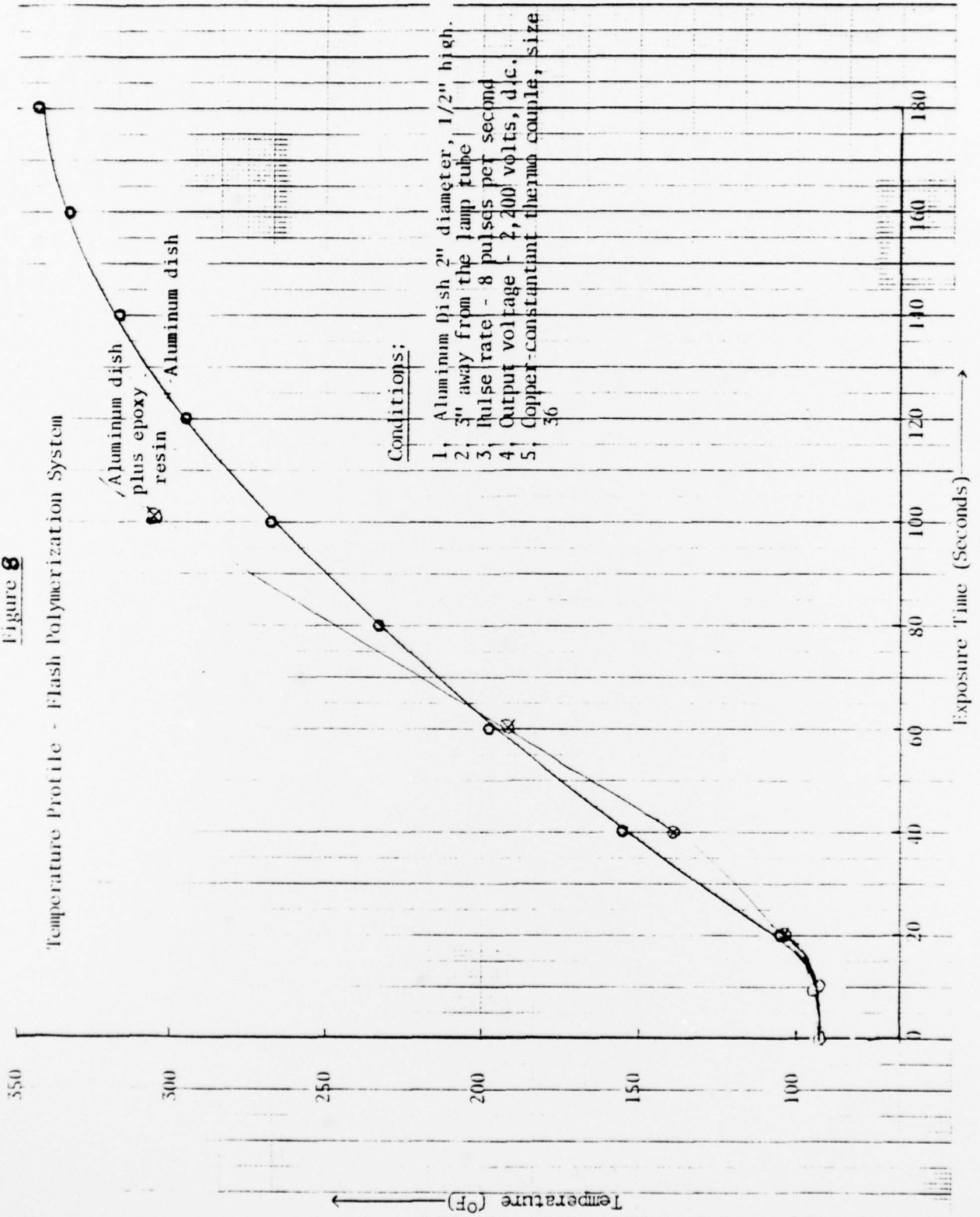


CONTRACT NO.		XENON CORP. MEDFORD, MASS.	
RELEASED	DRAWN	TITLE BLOCK DIAGRAM	
CHECKED	ENGINEER	SIZE	CODE IDENT NO. DRAWING NO.
E - IN - C	J.P.	A	-
MANAGER	APPROVED	SCALE	SHEET OF

FIGURE 7 TO BE INSERTED

Figure 8

Temperature Profile - Flash Polymerization System



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K&E 10 X 10 TO 1/2 INCH 7 X 10 SERIES
KUPFFEL & ESSER CO. MADE IN USA

TENSILE STRENGTH VS. TEMPERATURE OF GLASS CLOTH REINFORCED ROOM TEMPERATURE CURING EPOXY RESIN LAMINATES - HEAT AGING AT 200°C

Epoxy content 30% in laminate
(121 style glass cloth water A finish)

Epoxy composition:

Component A	GD19	50%
	MY73	140%
Component B	V40	7%



Figure 9.

TENSILE STRENGTH VS TEMPERATURE OF GLASS CLOTH REINFORCED ROOM TEMPERATURE CURING EPOXY RESIN LAMINATES - HEAT AGING AT 200°C

Epoxy content 32% in laminate
(18) style glass cloth under A Series

Epoxy composition:

Component A 6010 60%
 0500 14%
 Cokolat 6%

Component B Jeffamine Daws 84g
 Jeffamine Dico 54g

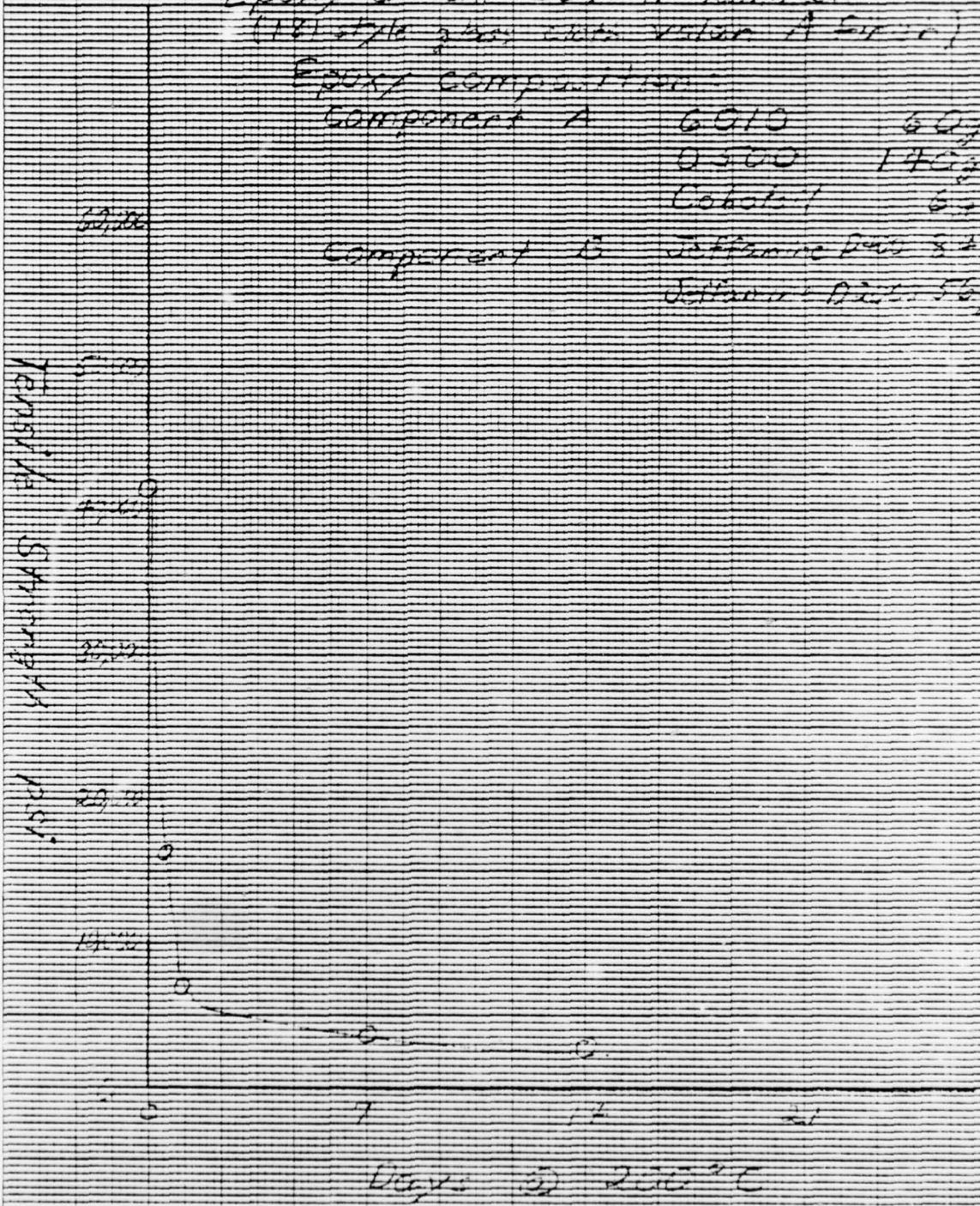


Figure 10.

46 1326

162 10 X 10 TO 3/4 INCH 7 X 10 INCHES
 NEUFEL & ESSEN CO. MADE IN U.S.A.

TENSILE STRENGTH VS TEMPERATURE OF GLASS CLOTH REINFORCED ROOM TEMPERATURE CURING EPOXY RESIN LAMINATES - HEAT AGING AT 200°C

Epoxy content: 30% in laminate
 (1st style glass cloth woven A finish)
 Epoxy composition:

Component A	6010	60%
	M772	40%
Component B	956	70%

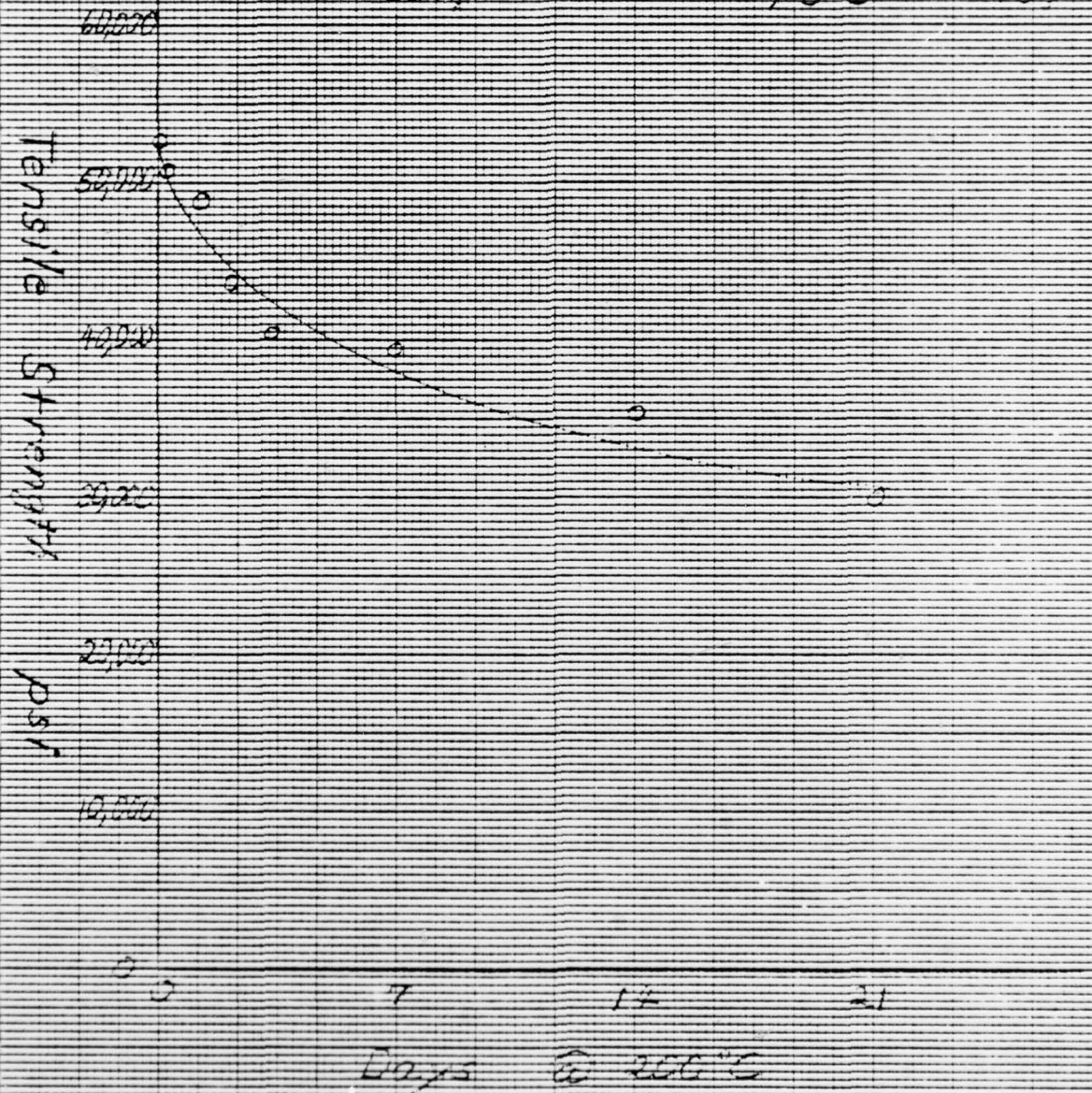


Figure 11.

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K-E 10 X 10 TO 15 INCH / X 10 100 HES
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