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LAMINATE STRENGTH CHANGES AFTER
TEN-YEARS AGING

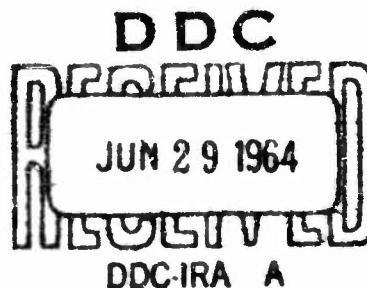
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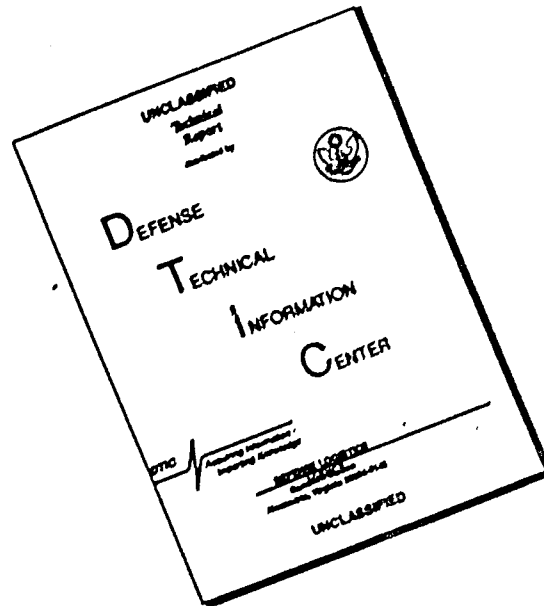
24 APRIL 1964

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LAMINATE STRENGTH CHANGES AFTER TEN-YEARS AGING

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ABSTRACT: This report contains flexural strength data showing the effects of ten-year aging on epoxy and polyester laminates.

Small reductions in strength were noted in 18 of the 20 cases where comparisons could be made. Epoxy and polyester laminates maintained their strength properties equally well.

Modulus values for the epoxy laminates were reduced in all but one case in amounts from 5 to 16%. The aging effect on the modulus of polyester laminates, on the contrary, was to increase the values from three to 13%.

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This is an interim report on the effects of twenty-year aging on the flexural strength properties of epoxy and polyester glass fabric laminates. Data presented here were obtained in 1963 on laminates made in 1953. Remaining specimens from these specimens will be tested in 1973.

The results indicate that ten-year aging in a normal laboratory environment has relatively unimportant effects on either flexural strength or modulus. All strength values obtained were still substantially higher than required by MIL-P-9300 (1955) and MIL-P-1813 B(1955) specifications.

The research reported herein was performed under NOL Rela-101-2-53(1953) and PR-4(1963).

The final report on this research must await testing of the remaining specimens in 1973.

R. E. ODENING
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By direction

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INTRODUCTION

Reinforced plastics are a relatively new class of materials. It has been only about 20 years since their first use in radomes. They are now widely used by the military due to a unique combination of properties such as light weight, high strength, dielectric transparency, non-corrosivity, low coefficient of thermal conductivity, and magnetic insensitivity. Their strength properties have been substantially increased since their first use as a result of improved resins, better glass fibers, more effective fiber finishes, and refined fabrication techniques.

There are many military applications where high strength properties and light weight are the prime considerations. Experience has shown, contrary to experience with concrete, that the strength properties of reinforced plastics as fabricated decrease with time. This is particularly true in moist and high temperature environments but also occurs to some extent under more moderate conditions.

Because of the relatively short history on these materials, there is not much data on the long-term effects of simple aging. Most of the studies on permanence of strength properties has been of the accelerated type with more emphasis on the effect of environment rather than on aging per se.

The major finding in this study is that simple aging for ten years has little effect on flexural strength properties of laminates made with epoxy and polyester resins.

Test specimens still remain from these laminates and these have been set aside to be tested in 1973 (after 20 years).

MATERIALS

All laminates were made from style 181 glass fabric treated with many different finishes so as to be compatible with different resin systems. The resins used were Epon 828 and four polyesters; Paraplex P-43, Plaskon 941, Selectron 5003, and Hetron 92. Details are given in Appendix A.

EXPERIMENTAL

All of the laminates were carefully made using, with one exception, vacuum impregnation of the resin. The details of the combinations of finish and resin and the manner of cure are given in Appendix B.

The methods of testing are given in Appendix II of NAVORD Report 6705 (1959). Simple aging as used in this report means that the uncut laminates were exposed to a $50 \pm 5\%$ relative humidity and $23 \pm 2^\circ\text{C}$ environment for at least 10 years.

RESULTS

Data on the effect of ten-year aging of epoxy laminates are tabulated in Table 1. These same data are graphically shown in Figures 1 and 2 in which the changes in dry and wet flexural strength respectively are evident.

The corresponding data from the polyester laminates are given in Table 2 and Figures 3 and 4.

In nine out of ten cases dry flexural strengths decreased. Most of these reductions were small but in one instance it was 15 1/2%. Reductions in wet strength were observed also in nine out of ten cases and these ranged from five to 16%.

The results show as a whole that even with the state-of-the-art in 1953 that simple ten-year aging has relatively insignificant effects on flexural strength properties. This is generally true for laminates made with fabrics having a variety of finishes and using different resins.

Additional flexural strength data on laminates for which no duplicates were made are shown in Table 3. These laminates were made in 1953 and tested in 1963. While no direct comparisons can be made against the strengths as made, the values shown indicate that the laminates still had very good strengths after ten years.

DISCUSSION OF RESULTS

Laminates 164-1 and 164-2 were made with epoxy resin and Volan A finished glass fabric (Table 1). Ten-year aging shows only three and six percent reductions in dry and wet strengths respectively. This is, perhaps, not real either since these data were obtained on different laminates which are of course duplicates. The averages shown for the 164-2 laminate are based on only three specimens each. This was done to save specimens for testing in 1973. The averages in this case are, however, meaningful since vacuum impregnation led to very small scatter in values for all laminates made in this fashion.

One of the original objects in the 166 series of epoxy laminates was to determine the effect of resin content on flexural strength, particularly when the laminate thickness was less than the sum of the thicknesses of 12 plies of dry fabric. The laminates 166-2 and 166-2D were pressed to a thickness of 0.098 which was 0.006 less than the nominal thickness of 12 plies of 181 style fabric. Laminates 166-4 and 166-4D were pressed to 0.108 and the pair 166-5 and 166-5D to a thickness of 0.114.

The 12 plies of fabric in the 166-2 pair of laminates should act like a compressed spring mattress to produce an interlaminar condition of constant stress. This stress condition might be relieved over a period

of time by either delamination or creep in the resin. The data in Table 1 clearly show that the largest loss in dry strength occurred when we press to a thickness less than nominal thickness of the cloth in the laminate. The data for 166-4 and 166-4D indicate that best permanence of dry flexural strength was obtained from laminating to a thickness of three to four percent greater than the nominal thickness of the fabric. The wet flexural strengths after ten years were, however, almost identical for all three thicknesses which was unexpected. All of the 1953 data, both dry and wet, show the usual decreasing strength with increasing resin content.

Platen stops were used to control laminate thickness. The resin contents for these laminates vary in a way which is puzzling. It is not reasonable to ascribe the different resin contents to voids either since the laminates were laid up using vacuum impregnation.

The first four sets of polyester laminates in Figure 3 show the expected effect on strength of increasing resin content. These were also laminated to different thicknesses. Laminates 167-1 and 167-1D show no loss in strength over ten years even though they were laminated to a thickness of only 0.096 (nominal thickness of cloth was 0.102). The next three sets of laminates show small decreasing dry strengths both as made and after ten years with increasing resin contents. The 1953 wet strengths of these same four sets (Fig. 4) show at most a nine percent decrease as resin content increases from 27.0 to 35.1%. The 1963 wet strength data fell off from 12 to a maximum of 16% below the 1953 values. Part of this may be due to real laminate differences since these comparisons are made between laminates which were duplicates. Averages are also based on three to four specimens, but again the uniformity of specimen values from vacuum-impregnated laminates is very good. There was in this instance, good correlation between laminate thickness and resin content.

The data for laminates 180-5 and 180-6 indicate no change in dry and wet flexural strengths as a result of ten-years aging. These again were duplicate laminates made with the polyester resin Selectron 5003 using an ATC (high temperature) catalyst cure. If the duplicates originally had the same dry and wet strengths, then this represents the only system that was completely resistant to deterioration in strength over a ten-year period under these environmental conditions. The fiber treatment in this case was the Bjorksten finish. The level of strength was, however, only moderate.

The laminates L-89-5 and L-89-6 were duplicates made in 1955 with the chlorinated polyester resin, Hetron 92. A period of eight-year aging showed decreases of 19 and 13% decreases in dry and wet flexural strengths respectively. These decreases could of course have been all, or in part, due to the fact the laminate tested in 1955 was different from the one tested in 1963. The resin content for the duplicate tested

in 1955 was 34% and the one in 1963, 33%. On the basis of this we would have expected, aging having had no effect, that the latter strength would have been a little higher rather than lower.

There were no duplicate laminates for the laminates shown in Table 3 all of which were made in 1953. No comparisons can, therefore, be made as before. The levels of strength after ten years are very good and well in excess of present Military Specification requirements. Specimens have been set aside for testing in 1973.

The modulus decreased with aging for all the epoxy laminates (Table 1). The amount was usually about five percent but in two cases the reduction was 16%. Of the 12 comparisons which could be made with polyester laminates (Table 2), the modulus decreased in only one instance (3%), was unchanged in one case, and, in all other cases increased by amounts from three to 13%. These data show clearly that resin system is more important than finish in determining the course of modulus on simple aging.

CONCLUSIONS

The effects from ten-year aging on flexural strength of laminates were smaller than anticipated. The greatest reduction in strength was 16% which was for a polyester laminate when tested after a period of two hours in boiling water. The data show Volan A, NOL-24 and the Bjorksten finishes on glass fabric to be similar in their reaction to aging in a laminate. There is no dramatic effect of resin system in terms of aging effects either. It seems, within the limitations of interpretation of data on duplicate laminates, that three polyester resins are fully as effective after ten years as an epoxy resin. Laminate modulus in flexure decreases slightly with epoxy resins and increases slightly with polyester resins.

RECOMMENDATIONS

It is recommended that the remaining untested flexural specimens from these laminates be tested in 1973 and the results compared as far as possible with those shown in Tables 1, 2 and 3. Testing should be done as described in Appendix II of NAVORD 6705 (1959).

TABLE 1
EFFECT OF TEN-YEAR AGING ON EPOXY LAMINATE STRENGTH^{a, b}

Laminate Number	Year Tested	Finish	Curing Agent	Ave. Dry Flex. Str. ^c Kg/cm ²	Ave. Wet Flex. Str. ^c Kg/cm ²	Ave. Dry Modulus ^c Kg/cm ² X 10 ⁻⁵	Ave. Wet Modulus ^c Kg/cm ² X 10 ⁻⁵	Resin Content %	Rockwell (M)	1973 ^e
164-1	1953	Volan A	D	6290 (4) ^d	5070 (4) ^d	2.82	2.54	31.4	-	0
164-2	1963	Volan A	D	6100 (3)	4760 (3)	2.68	2.50	30.8	109	6
166-2D	1953	NOL-24	A	7680 (3)	6930 (4)	3.38	3.10	-	116	0
166-2	1963	NOL-24	A	6480 (3)	5970 (4)	2.82	2.61	32.9	116	6
166-4D	1953	NOL-24	A	7250 (4)	6410 (4)	2.89	2.68	29.0	116	0
166-4	1963	NOL-24	A	6810 (2)	5980 (3)	2.74	2.54	31.6	116	6
166-5D	1953	NOL-24	A	6580 (4)	6160 (4)	2.68	2.61	32.7	116	0
166-5	1963	NOL-24	A	6180 (3)	5840 (4)	2.54	2.32	34.7	115	7

a. Respective pairs of laminates were duplicates; Epon 828 resin was used.

b. Flex. strength data shown graphically in Figures 1 and 2.

c. Number of specimens available for testing in 1973.

d. Total number of specimens in average shown in parenthesis.

e. To convert to psi, multiply by 14.21.

TABLE 2
EFFECT OF TEN-YEAR AGING ON POLYESTER LAMINATE STRENGTH^a

Laminate Number	Year Tested	Finish	Resin	Curing System	Ave. Dry Flex. Str. d Kg/cm ²	Ave. Wet Flex. Str. d Kg/cm ²	Ave. Dry Mod. d Kg/cm ² X 10 ⁻⁵	Ave. Wet Mod. d Kg/cm ² X 10 ⁻⁵	Resin Content, %	Rockwell (M)	1973 ^c
167-1D	1953	BJT	P-43	DDM and Nuodex	6560 (4) ^b	6380 (4) ^b	2.68	2.61	27.0	116	0
167-1	1963	BJT	P-43	DDM and Nuodex	6600 (4)	5590 (4)	3.02	2.68	27.3	114	0
167-2D	1953	BJT	P-43	DDM and Nuodex	6790 (4)	6450 (4)	2.68	2.68	30.8	116	0
167-2	1963	BJT	P-43	DDM and Nuodex	6490 (3)	5620 (4)	2.82	2.61	29.5	112	7
167-5D	1953	BJT	P-43	DDM and Nuodex	6400 (4)	6050 (4)	2.46	2.40	32.8	116	0
167-5	1963	BJT	P-43	DDM and Nuodex	6040 (3)	5060 (4)	2.61	2.40	35.1	114	7
167-6D	1953	BJT	P-43	DDM and Nuodex	5980 (4)	5990 (4)	2.40	2.40	35.5	115	0
167-6	1963	BJT	P-43	DDM and Nuodex	5870 (3)	5250 (4)	2.61	2.46	35.1	114	0
180-5	1953	BJT	Selectron 5003	ATC	5710 (4)	4970 (4)	2.40	2.25	30.9	116	0
180-6	1963	BJT	Selectron 5003	ATC	5610 (3)	5090 (3)	2.61	2.46	31.2	114	7
L-89-5	1955	MOL-24	Betron 92	DDM and Nuodex	6780 (2)	5980 (2)	2.46	2.31	34.0	-	0
L-89-6	1963	MOL-24	Betron 92	DDM and Nuodex	5920 (4)	5170 (5)	2.75	2.54	33.0	111	8

a. Respective pairs of laminates were duplicates.

b. Number in parenthesis is the number of specimens tested.

c. Number of specimens available for testing in 1973.

d. To convert to psi, multiply by 14.21.

TABLE 3
LAMINATE STRENGTHS AFTER TEN YEARS^a

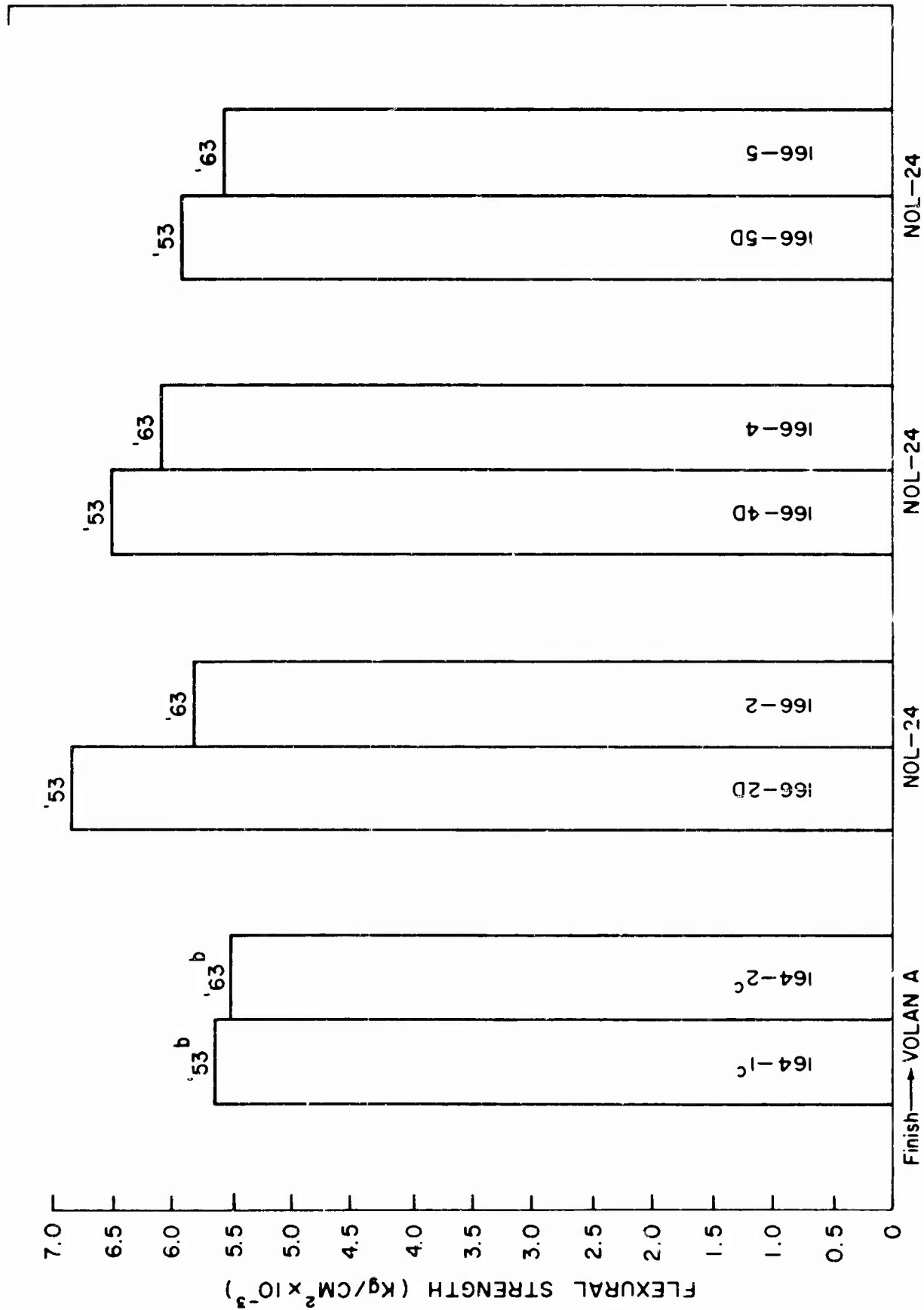
Laminate Number	Year Tested	Finish	Resin	Curing System	Ave. Dry d Flex. Str. $\frac{Kg}{cm^2}$	Ave. Wet d Flex. Str. $\frac{Kg}{cm^2}$	Ave. Dry d Modulus $\frac{Kg}{cm^2} \times 10^{-5}$	Ave. Wet Modulus $\frac{Kg}{cm^2} \times 10^{-5}$	Resin Content, %	Rockwell (M)	(1973) ^c
164-4	1963	WOL-24	Epon 828	A	6560 (3) ^b	6100 (4) ^b	2.96	2.68	31.6	114	7
164-6	1963	WOL-25	Epon 828	A	6470 (3)	5130 (3)	2.82	2.32	30.5	114	7
164-8	1963	WOL-18	Epon 828	A	6110 (3)	5290 (4)	2.75	2.46	29.8	114	7
180-1	1963	BJY	Plaskon 941	ATC	4950 (3)	5040 (4)	2.99	2.60	23.9	112	6
180-2	1963	BJY	Plaskon 941	ATC	6070 (3)	5530 (3)	2.75	2.54	29.8	115	7
180-3	1963	BJY	Plaskon 941	ATC	5500 (3)	4920 (4)	2.60	2.46	30.1	113	6
180-4	1963	BJY	Plaskon 941	ATC	5550 (3)	5090 (4)	2.82	2.68	24.7	113	7

a. No duplicate laminates made for testing in 1953.

b. Numbers in parenthesis show number of specimens tested.

c. Total number of specimens remaining for testing in 1973.

d. To convert to psi, multiply by 14.21.



a. See Table 1 for details.
 b. Year in which laminate was tested.
 c. Laminate identification.

Fig 1. EFFECT OF AGING ON EPOXY LAMINATE DRY STRENGTH^a

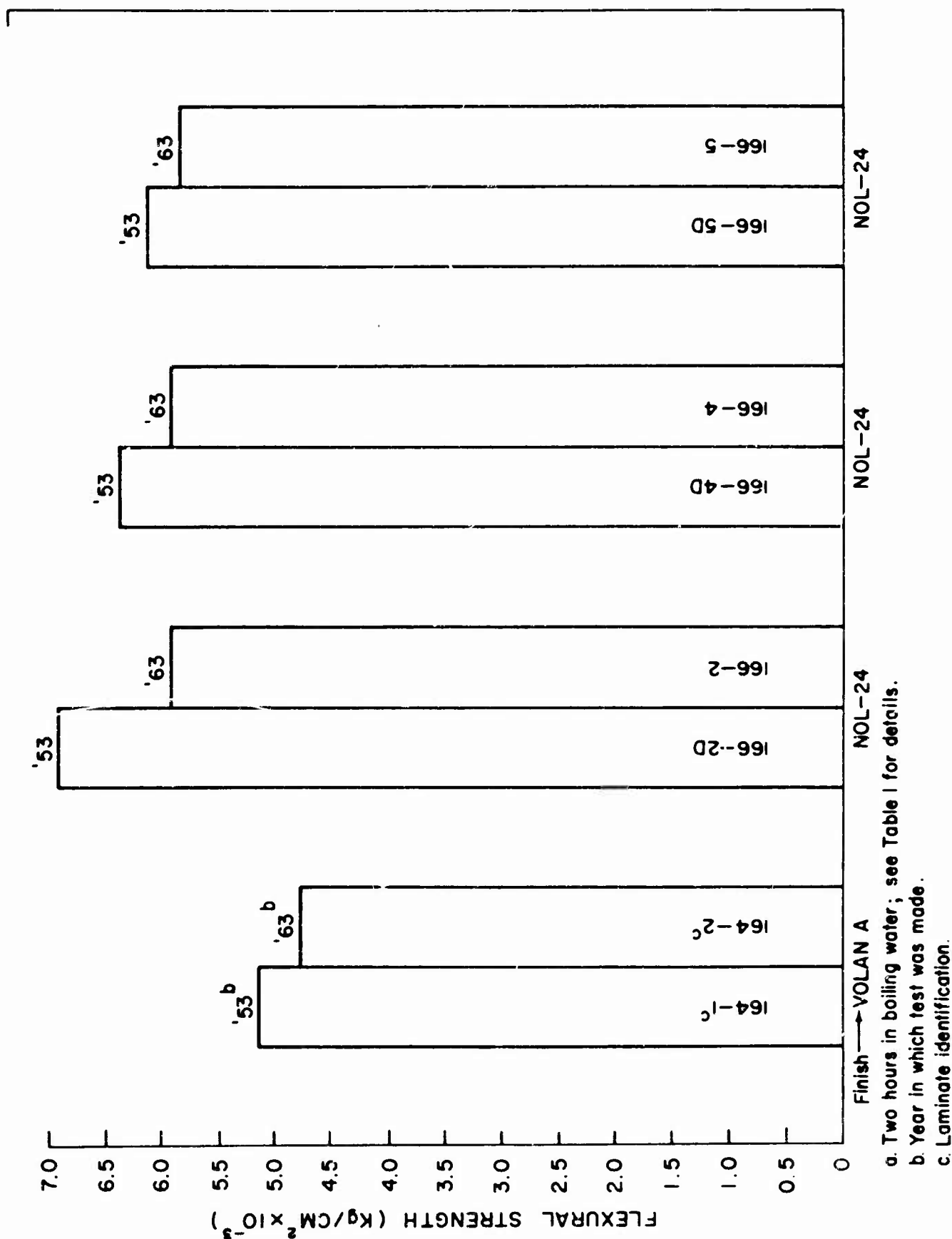
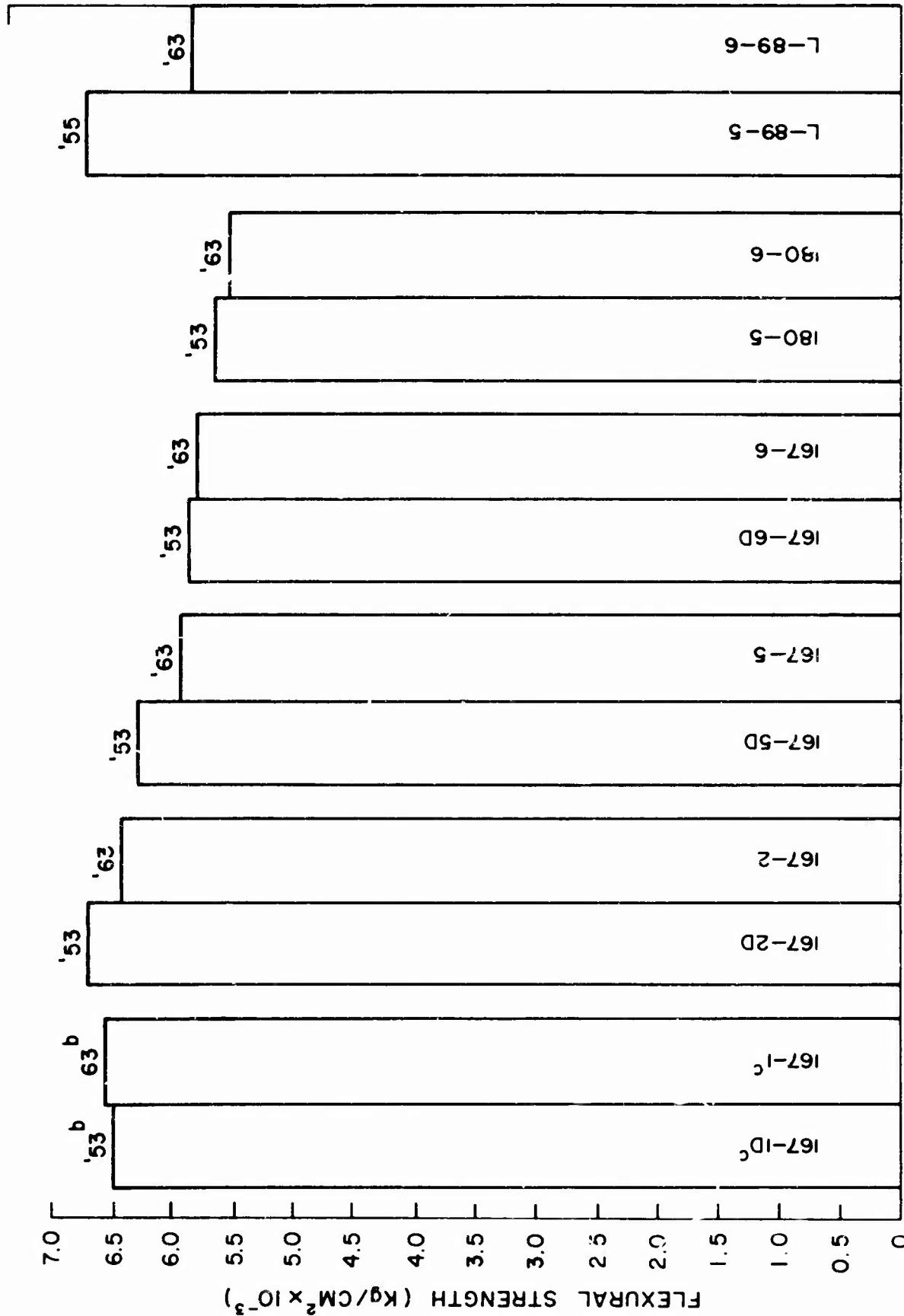
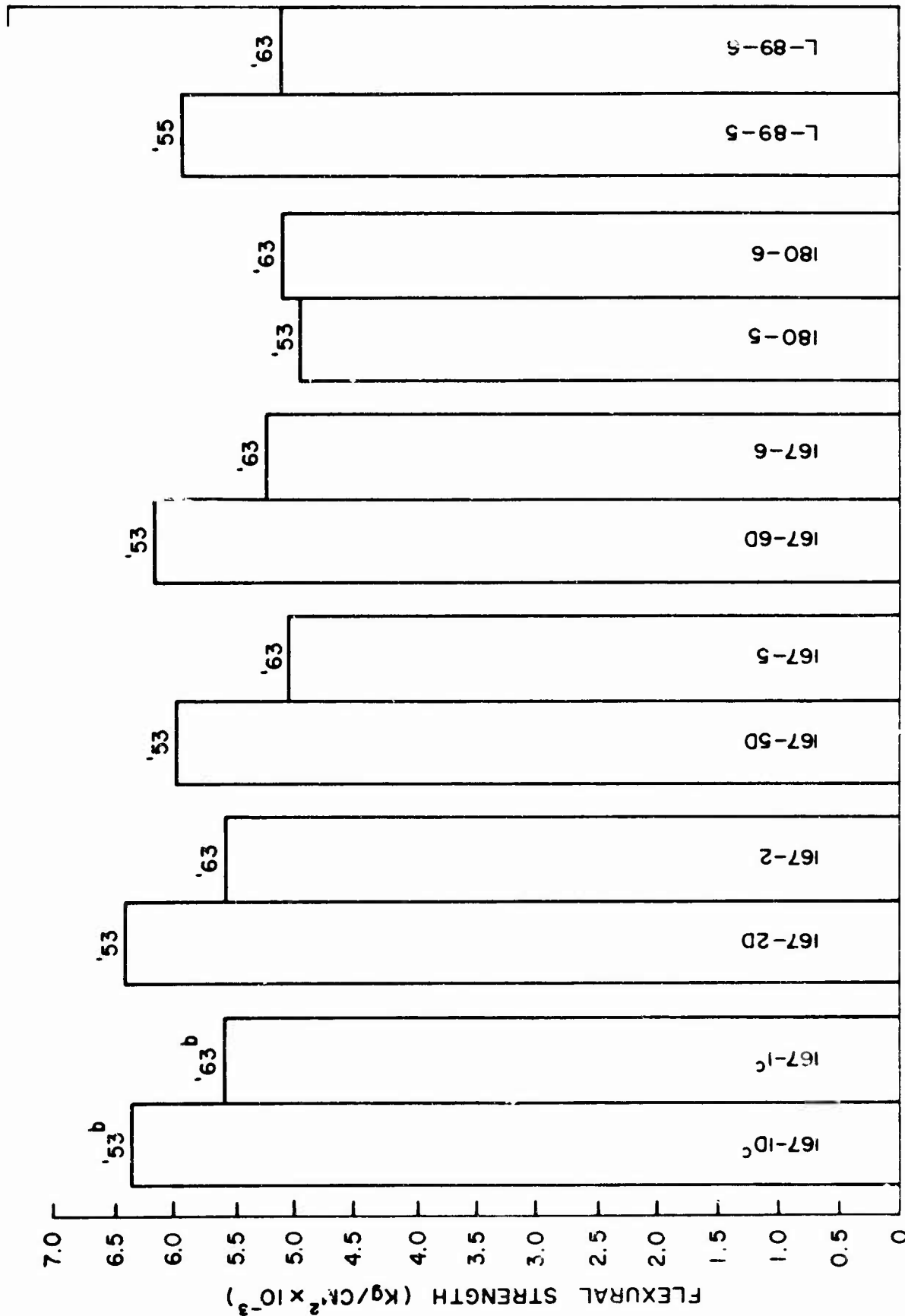


Fig. 2. EFFECT OF AGING ON EPOXY LAMINATE WET STRENGTH^o



- a. See Table 2 for details.
- b. Year in which laminate was tested.
- c. Laminate identification.

Fig. 3. EFFECT OF AGING ON POLYESTER LAMINATE DRY STRENGTH^o



a. Two hours in boiling water; see Table 2 for details.

b. Year in which test was made.

c. Laminate identification.

Fig. 4. EFFECT OF AGING ON POLYESTER LAMINATE WET STRENGTH⁰

APPENDIX A

MATERIALS

A-1. Fabric and Finishes. All the laminates were made with style 161 glass fabric with different finishes as follows:

a. Volan A finished fabric; supplied by United Merchants Industrial Fabrics, 1407 Broadway, New York 18, New York.

b. BJY finished fabric; supplied by the Bjorksten Research Laboratories, Madison, Wisconsin (NAVORD Report 2802).

c. NOL-24 finished fabric for laminate 164-4; originally 181-111 (starch) fabric believed to have been supplied by Deering Milliken and Co., 240 Church Street, New York 13, New York. This cloth was heat-cleaned for eight hours at 400°C and then given a NOL-24 treatment according to the procedure in NAVORD 3811. NOL-24 was the product from the reaction of equimolar amounts of allyltrichlorosilane and resorcinol.

d. NOL-24 finished fabric for laminates 166-2, 166-2D, 166-4, 166-4D, 166-5 and 166-5D; originally 181-111 (starch) fabric from Deering Milliken and Co. This cloth was heat-cleaned at 480°C for eight hours and then given a NOL-24 treatment as in c. above.

e. NOL-24 finished fabric for laminates L-89-5 and L-89-6; original fabric was supplied by United Merchants Industrial Fabrics with treatment 112 (heat-cleaned). This was given a NOL-24 treatment with lot S-8 of NOL-24 reagent to check it out for pilot plant use. This treatment was designated T-5-A and was carried out under carefully controlled conditions.

f. NOL-25 finished fabric for laminate 164-6; this was originally the same cloth as in c. above except this had been given a NOL-25 treatment according to the procedure in NAVORD Report 3811. NOL-25 was the product from the reaction of equimolar amounts of allyltrichlorosilane and phenol.

g. NOL-18 finished fabric for laminate 164-8; this was originally the same fabric as in c. above except this had been given a NOL-18 treatment according to the procedure in NAVORD Report 3811. NOL-18 was the product from the reaction of equimolar amounts of allyltrichlorosilane and glycidylmethacrylate.

A-2. Resins

a. Paraplex P-43; polyester resin supplied by Rohm and Haas Co., Washington Square, Philadelphia 5, Pennsylvania.

b. Epon 828; epoxy resin supplied by Shell Chemical Co., 380 Madison Avenue, New York 17, New York.

c. Selectron 5003; polyester resin supplied by the Pittsburgh Plate Glass Co., 420 Ft. Duquesne Blvd., Pittsburgh 22, Pa.

d. Plaskon 941; polyester resin supplied by Allied Chemical, Plastics Division, 40 Rector Street, New York 6, New York.

e. Estron 92; chlorinated polyester resin supplied by the Hooker Chemical Corp., Niagara Falls, New York.

A-3. Curing Agents, Etc.

a. Curing Agent A; diethylaminopropylamine supplied by Shell Chemical Co.

b. Curing Agent D; tri(dimethylaminomethyl)phenol tri(2-ethyl hexoate) supplied by Shell Chemical Co.

c. Lupersol DDM and Luperco ATC; peroxide catalysts supplied by the Lucidol Division of Wallace and Tiernan, Inc., 1740 Military Road, Buffalo, New York.

d. Nuodex; a six percent solution of cobalt naphthenate supplied by the Nuodex Products, Inc., Elizabeth, New Jersey.

APPENDIX B

EXPERIMENTAL

B-1. All laminates except L-89-5 and L-89-6 were made in 1953. Some were made to study creep properties when loaded under water at a low level of stress for long periods of time. Others were made to study the interaction among variables such as resin content, finish, and resin system, in terms of flexural strength as well as creep. In some cases duplicate laminates were made which were tested simply for flexural properties in 1953. In other cases, no duplicates were made and as a result there are no 1953 data for comparison (Table 3). Due to a combination of circumstances, the original intent of this program was not carried out.

B-2. In 1962, it was decided to hold the remaining laminates from the program for another year and to test them in flexure at approximately ten years after their fabrication. These laminates were cut into test specimens in 1963. In order to expand the aging tests for another decade, only half of these specimens were tested, the rest being set aside for testing in 1973.

B-3. The fabrication of all the laminates made in 1953 is described in NOL Notebook 80-3750. The details on L-89-5 and L-89-6, which were made in 1955, are described in Notebook 96-4699.

B-4. With the exception of the 1955 laminates, all were made using vacuum impregnation as described in NAVORD Report 3889. The 12 plies of style 181 fabric were, in all cases, "nested" in such a fashion that the warp yarns were parallel.

B-5. Laminates 164-1 and 164-2 were duplicates which were made with Epon 828 using 11 1/2% of curing agent D. The fabric had a Volan A finish. The curing cycle consisted of 60' at 74°C followed by 30' at 115°C. Platen stops were used to control resin content.

B-6. Laminates 164-4, 164-6, 164-8, 166-2, 166-2D, 166-4, 166-4D, 166-5 and 166-5D were also made with Epon 828 but in this case cured with 5.65% (6 PHR) of curing agent A. The curing cycle was the same as above and platen stops were used. Laminates 167-2 and 166-2D, etc. were duplicates, the "D" denoting this. The details on finishes used are shown in Tables 1 and 3.

B-7. The polyester laminates 167-1 and 167-1D, 167-2 and 167-2D, and 167-5 and 167-5D were respectively duplicates. BJI finished fabric was used. The resin system was Paraplex P-43 cured with one percent of DDM and one percent of Nuodex (Cobalt 6%). The cure consisted of at least three hours at room temperature (about 24°C) followed by three hours at 55°C. Platen stops were used.

B-8. Laminates 180-1, 180-2, 180-3 and 180-4 were also made with BJJ finished cloth. The resin system was Plaskon 941 cured with two percent of Luperco ATC catalyst. The curing cycle consisted of 30' at 82°C followed by 30' at 121°C and again platen stops were used. Laminates 180-5 and 180-6 are similar to those except Selectron 5003 resin was used.

B-9. The Laminates L-89-5 and L-89-6 were made in 1955. The fabric used was finished with NOL-24 and the lot was denoted T-5-A. The resin system was the chlorinated polyester, Hestron 92, with 1/4% of DDM and 1/10% of Nuodex. The impregnation was carried out in open air by placing the assembled plies on top of a pool of the warmed resin and letting it wick up into the lay-up. The method is described in NAVORD Report 6705. The first step of the cure consisted of placing the lay-up in the press overnight at room temperature. This was followed by a post-cure in an oven for 16 hours at 60°C. Platen stops were not used. Laminate L-89-5 was tested in 1955 while laminate L-89-6 was tested in 1963 and will be further tested in 1973.