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WADC TECHNICAL REPORT 52-156

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IMPROVED STRUCTURAL ADHESIVES FOR BONDING METALS

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H. C. ENGEL
BLOOMINGDALE RUBBER COMPANY

7
DECEMBER 1952

WRIGHT AIR DEVELOPMENT CENTER

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WADC TECHNICAL REPORT 52-156

IMPROVED STRUCTURAL ADHESIVES FOR BONDING METALS

H. C. Engel
Bloomington Rubber Company

December 1952

Materials Laboratory
Contract No. AF 33(038)-21669
RDO No. 604-302

Wright Air Development Center
Air Research and Development Command
United States Air Force
Wright-Patterson Air Force Base, Ohio

FOREWORD

This report describes the work performed by Bloomingdale Rubber Company under Contract No. AF 33(038)-21669, Research and Development Order No. 604-302, "Structural Adhesives", for the period 6 March 1951 to 1 April 1952. The project was administered under the direction of the Structural Design Data Branch, Materials Laboratory, Directorate of Research, Wright Air Development Center, with Major T. J. Martin acting as project engineer.

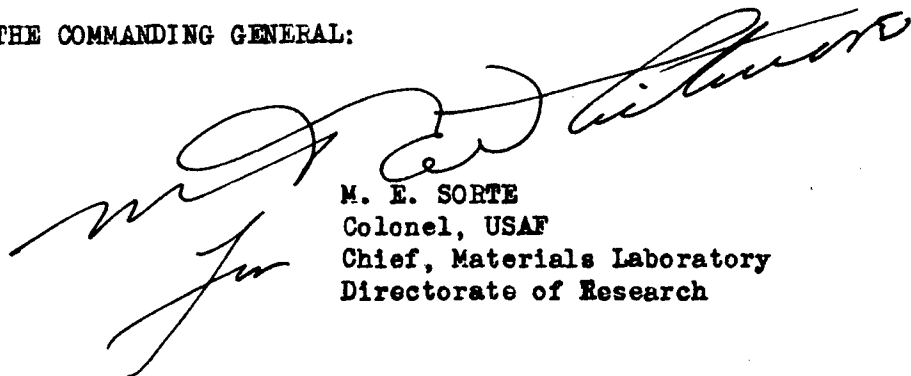
ABSTRACT

Work under USAF Contract No. AF 33(038)-21669 has been directed toward the development of an improved structural adhesive for bonding metals. An adhesive designated as PA-101, developed and tested under this contract, meets most of the research objectives and so far as is now known conforms to the requirements of Specification 14164. The PA-101 formulation has been evaluated as a two-part, liquid adhesive.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDING GENERAL:

A large, stylized handwritten signature in black ink, likely belonging to M. E. Sorte, is written over the typed name and title.

M. E. SORTE
Colonel, USAF
Chief, Materials Laboratory
Directorate of Research

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I. INTRODUCTION

This report is a general summary of the work on Research Contract AF 33(038)-21669 from April 1, 1951 to April 1, 1952. It reviews the experimental work done and discusses formulation, manufacture and properties of the cement developed.

II. RESEARCH OBJECTIVES

Research objectives as contained in Exhibit A of the contract and, as more fully amplified by later conferences between the Contractors' and the Materials Laboratories' representatives, may be summarized as the development of an adhesive having a maximum of the desirable characteristics outlined below:

- (1) Strength and durability characteristics to conform with Specification 14164.
- (2) Required curing temperatures and pressures should allow user relatively wide latitude to facilitate production.
- (3) The adhesive should be capable of production under practical conditions in unlimited quantities, and preferably with readily available commercial equipment. Critical manufacturing variables should be held to a minimum.
- (4) Application characteristics to be superior to those of best commercial present day adhesives. Adhesive should preferably be available as 100% solids or as a film which does not require a companion primer having critical application requirements.
- (5) Metal cleaning methods should be simple and non-critical to facilitate production of reliable bonds.
- (6) The adhesive should be not only non-corrosive on all common metals, including magnesium, aluminum and ferrous alloys, but should as a film afford substantial protection to the metal against corrosion.

In a word, this program was aimed at the development of an adhesive equal to or better than present commercial adhesives, but having sufficient latitude in bonding pressure, bonding temperature, film thickness, and surface cleanliness requirements to simplify manufacturing methods and to aid in the development of consistent bond strength and environmental resistance properties.

III. SUMMARY AND CONCLUSIONS

The adhesive designated in this report as PA-101, developed under Research Contract AF 33(038)-21669, has satisfactorily passed the requirements of this contract as outlined in the objective of this report. It has also satisfactorily met the strength requirements and fluid exposure resistance of U.S.A.F. Specification 14164 for all of the tests performed on bonds cured at 300°F and 250°F. Fatigue strength at standard and low temperature, Bend tests and Impact strength at standard and low temperature are yet to be run.

This cement is a two-part type consisting of Buna N synthetic rubber and phenolic resins compounded with suitable vulcanizing agents and accelerators for satisfactory cures at moderate temperatures of 200°F to 300°F. It may be manufactured by simple milling procedures sufficient for smooth blending of the batch and subsequent solution in methyl ethyl ketone solvent.

The aging characteristics of both part 1 and part 2 of PA-101 cement have been tested up to three months with satisfactory results.

Maximum bond strengths are obtained using 100 psi bonding pressure or higher; however 50 psi produces bonds which pass U.S.A.F. Specification 14164.

Several cleaning methods such as Sprex AC alkaline bath, acetone wipe and chromic-sulfuric acid etch result in bond strengths above 3800 psi at 76°F and above 2100 psi at 180°F for cures at 250°F and 300°F.

IV. EXPERIMENTAL METHODS

All test samples were prepared using .064 inch 24S-T 3 Alclad metal bonded at 1/2" depth of lap.

The metal was cleaned by first removing the excess oil and dirt by wiping with acetone. It was then immersed in a chromic-sulfuric acid solution for ten minutes at 160°F. The acid solution was composed of the following:

chromic acid flake 5 oz./gal.

Conc. sulfuric acid (technical) 23 oz./gal.

The metal was rinsed thoroughly in hot running water and dried in an oven.

Although other cleaning methods were tested in separate experiments, the above method was followed throughout the contract for all formula evaluations. Two brush coats of adhesive were applied to the metal within eight hours of the cleaning operation. The adhesive was air dried for sixteen hours followed by an oven dry of one hour at 150°F. The test panels were assembled and cured in an electrically heated platin press at a bonding pressure of 100 psi according to the following temperature-time schedule:

<u>Temperature</u> <u>°F</u>	<u>Time in</u> <u>Minutes</u>
300	20
275	30
250	45
225	70
200	90

The cured glue line thickness was controlled at $0.003" \pm 0.0005"$ except where deliberately varied for test purposes.

Cured test panels were cut into one inch wide coupons numbered consecutively across the panel. All tests were conducted on a Dillon Testing Machine using a loading rate of 600 to 700 psi per minute. Tests at 180°F were conducted by enclosing the upper part of the testing machine in an insulated and heated cabinet. A similar cabinet packed with dry ice was used for tests at -70°F. All temperatures were measured by means of a thermo-couple clamped to the

specimen at the glue line. The ultimate load was determined to the nearest 5 pound increment. The length and width of each bond area was measured to the nearest 0.01 inch and the shear stress in the adhesive calculated in pounds per square inch for each test coupon.

V. DISCUSSION

The first experimental studies were conducted on formulations based on poly acrylic rubber-phenolic resin blends. Forty-six formulations consisting of Hycar PA-21 and various commercial phenolic resins with several vulcanizing systems were tested. Although several cements were developed of this general type which gave bond strengths over 2500 psi when cured at 200°F and over 3000 psi when cured at 300°F, the strength at -70°F was uniformly poor (below 800 psi) due to the embrittlement of the poly acrylic rubber constituent. Therefore this line of investigation was shifted to nitrile rubber-phenolic resin formulations.

Of the nitrile rubber types available Hycar OR-25ST was selected because of its ready solubility in common solvents, simple milling procedure requirements, good solution stability, and satisfactory strength properties over a wide temperature range. The formulation studies conducted were aimed at (a) selection of satisfactory phenolic resins, (b) development of a vulcanization system capable of curing below the 325°F temperature normally used, (c) reasonable stability of solutions containing so reactive a system, (d) satisfactory filler reinforcement.

A total of sixty-two cement formulations based on nitrile rubber Hycar OR-25ST were studied. Since the vulcanization system required for curing at 200°F and 250°F was also reactive at normal temperatures and therefore affected solution stability a two-part cement formulation was necessary. The more reactive phenolic resins satisfactory for curing at low temperatures with the nitrile rubber were also found to be mutually reactive in the same solution and hence resulted in lowered bond strength after solution aging of the rubber and phenolic resins together. Since bond strength at -70°F of the nitrile rubber cements studied were uniformly high, no formulation modification was necessary in order to meet this requirement. Therefore the nitrile rubber and phenolic resins were kept in separate parts and each of the remaining constituents such as carbon black filler, zinc oxide, stearic acid, sulfur, Agerite Resin D, Captax and Butyl Eight were tested for stability after aging with either the rubber or the phenolic resins. Satisfactory solution stability in methyl ethyl ketone was obtained by milling the rubber sufficiently to blend the carbon filler, the stearic acid, zinc oxide and Agerite Resin D. However, it was found that the accelerator Butyl Eight was not stable when mixed with the phenolic resin as Part 2 of the cement, but remained stable in the rubber solution provided no sulfur or Captax were present. The sulfur and Captax were finely ground and dispersed thoroughly in the powdered phenolic resins. This latter mixture, stable in dry powder form, is then added to the rubber solution at the time of use. This cement, designated PA-101, is prepared as follows:

<u>PART 1</u>	
<u>Constituent</u>	<u>Parts by weight</u>
1. Hycar OR-25ST	100 Band on cold rolls.
2. Pilletex Carbon black SRF	50 Add to rubber and mill 16 minutes.
3. Stearic acid	1 Add items 3, 4 and 5 and mill for 5 minutes.
4. Zinc Oxide	5

PART 1 (Cont'd)

<u>Constituent</u>	<u>Parts by weight</u>	
5. Agerite Resin D	1	Dissolve in methyl ethyl ketone at 20% solids.
6. Butyl EIGHT	7	Add to above solution.

PART 2

1. Bakelite 18773	50	Grind items 3 and 4 and thoroughly disperse
2. Durez 7031 A	50	with items 1 and 2 to form homogeneous dry powder.
3. Captax	2	
4. Sulfur	3	Sift

At the time of use 12.8g of Part 2 powder are added to 100g of Part 1 solution and stirred thoroughly for three to five minutes.

Tables 1 and 2 present the test data on PA-101 cured at 300°F and 250°F respectively and tested against the requirements of U.S.A.F. Specification 14164. The tests performed consisted of dry shear strength at 76°, 180°F and -70°F, shear strength at 76°F after 7 days immersion in isopropyl alcohol, ethylene glycol, hydraulic oil, hydrocarbon fluid and after 30 days immersion in water. Part of these data were previously presented in Report No. 11 but are repeated here in order to present the complete data obtained for this specification in the final report.

Samples for fatigue testing at 76°F and -70°F were prepared and forwarded to the Materials Laboratory, Wright Air Development Center.

Table 3 presents test data on samples prepared from metal cleaned by the following methods; (a) immersion in a Sprex AC alkaline solution for 10 minutes at 160°F; (b) wipe with clean cloth wet with acetone; (c) wash with soap and water; (d) immersion in Sprex AC alkaline solution followed by an acid etch in a chromic-sulfuric acid solution, 10 minutes at 160°F. Cleaning by wiping with acetone gave bond strengths of 3950 psi and 3850 psi at 76°F and 2175 psi and 2000 psi at 180°F for 300°F and 250°F cures respectively. These shear strengths compare very favorably with those obtained using chemical cleaning methods such as Sprex AC alkaline solution which gave 3945 psi and 4375 psi at 76°F, and 2250 psi and 2150 psi at 180°F. Sprex AC alkaline cleaner followed by a chromic-sulfuric acid etch resulted in bond strengths of 4000 psi and 4100 psi at 76°F and 2350 psi and 2115 psi at 180°F. Cleaning by soap and water resulted in definitely inferior adhesion. During the progress of the test program it was found that one variable which influenced the shear strength of the rubber based adhesives was the thickness of the glue line; therefore, this factor was controlled at .003 inch ± .001 inch in as much as possible on all test samples prepared using PA-65 cement and all subsequent formulas. A series of test panels was then prepared using PA-101 cement in which an attempt was made to obtain cured glue lines varying from .002 to .008 inch. Samples were made using from one to six brush coats of adhesive on each faying surface. However the heavier applications of adhesive did not result in thicker cured glue lines. This was due in all probability to the

increased flow (at equal pressure) of the thicker films. Examination of the data shows that the shear strength varies as a function of the number of coats of adhesive applied rather than in direct proportion to the cured glue line thickness. This may possibly be explained by greater solvent retention of the thicker film. Table 4 lists the detailed test data.

Table 5 gives the test data obtained from panels bonded at 50 psi as compared with two samples bonded at 100 psi. The lower bonding pressure caused a loss of 22 per cent in shear strength at 76°F and 16 per cent at 180°F.

Table 6 lists the average shear strength data on all adhesive formulas as developed on this contract for 300°F and 200°F or 250°F cures when tested at 76°F and 180°F. These formulas PA-45 through PA-108 were of the Buna N-Phenolic Resin type.

Tables 7 through 17 present all formulations studied during the contract and Table 18 lists and briefly describes all materials used in the various formulations.

Cement formulas PA-1 through PA-18, PA-22, 23, 24, 29, 33, 35 and 36 consisted of preliminary studies of simple blends of Hycar-PA 21 poly acrylic synthetic rubber with various phenolic resins for qualitative evaluation only, therefore these materials are not listed in the tables of cement formulas. Duplicate formulations occasionally appear, in some cases variations in milling procedures were used. The detailed variation used is described in the monthly reports. In other instances two-part cements were prepared with different placement of the ingredients in order to obtain optimum stability of the two parts.

All of the adhesives were prepared using methyl ethyl ketone solvent except as noted below. The solids content of the cements as mixed for application was 29.1 per cent. In PA-97 adhesive a solvent blend was used consisting of ethylene dichloride 40 parts, methyl ethyl ketone 40 parts and denatured alcohol 20 parts by weight.

In PA-80 and PA-81 a solvent blend was used consisting of ethylene dichloride 40 parts, toluene 40 parts, methyl ethyl ketone 6 parts, secondary butyl alcohol 18 parts and denatured alcohol 18 parts by weight.

Table 1TEST DATA OBTAINED ON PA-101 CEMENTCURED AT 300°F

Sample No.	Test	Specification Requirement psi	Shear strength of PA-101, psi
766-1	Shear	2500 min.	4200
-5	at		4400
-10	76°F		4250
767-1			4350
-5			4550
-10			4200
AV =			4325
766-2	Shear at	1250 min.	2450
767-2	180°F		2550
AV =			2500
766-3	Shear at	2500 min.	5050
767-3	-70°F		5450
AV =			5250
774-1	Shear at	2000 AV.	3890(Control-not
-2	76°F after		4100 immersed)
-3	7 days		4150
-4	immersion		4150
-5	in isopropyl		4200
-6	alcohol		4100
-7	(AN-F-13)		4200
-8			4300
-9			4000
-10			4000
-11			3950
AV =			4114
776-1	Shear at	2000 AV.	5990(Control-not
-2	76°F after		4050 immersed)
-3	7 days		4200
-4	immersion in		4350
-5	ethylene		4250
-6	glycol		4250
-7	(AN-E-2)		4255
-8			4240
-9			4210
-10			3900
-11			3800
AV =			4151

Table 1 Continued - TEST DATA OBTAINED ON PA-101 CEMENT CURED AT 300°F

778-1	Shear at	2000 Av.	4182
-2	76°F after		4050
-3	7 days		4150
-4	immersion in		4100
-5	hydraulic oil		4300
-6	(AN-O-366)		4350
-7			4200
-8			4200
-9			4210
-10			4200
-11			4100
AV. =			4185
780-1	Shear at	2000 AV.	3825(control -not
-2	76°F after		4315 immersed)
-3	7 days		4365
-4	immersion in		4365
-5	hydrocarbon		4365
-6	fluid		4215
-7			4315
-8			4460
-9			4170
-10			4115
-11			3970
AV. =			4265
772-1	Shear at	2000 AV.	4060
-2	76°F after		3645
-3	30 days		4220
-4	immersion in		4270
-5	water		4220
-6			3335
-7			4270
-8			4215
-9			4165
-10			3855
-11			3490
AV. =			3970
776-4	Long time	800 psi	315 hours no
	strength		failure
	at 180°F		

Table 2TEST DATA OBTAINED ON PA-101 CEMENTCURED AT 250°

Sample No.	Test	Specification Requirement psi	Shear Strength of PA-101. psi
768-1	Shear at 76°F	2500 min.	4100
-5			4400
-10			4000
769-1			4300
-5			4500
-10			4400
			AV. = 4300
768-2	Shear at 180°F	1250 min.	1950
769-2			1955
			AV. = 1952
768-3	Shear at -70°F	2500 min.	4850
769-3			5100
			AV. = 4975
775-1	Shear at 76°F after 7 days immersion in isopropyl alcohol (AN-F-13)	2000 Av.	4130(control -not)
-2			4110 immersed)
-3			4190
-4			4200
-5			4250
-6			4200
-7			4205
-8			4200
-9			4050
-10			4050
-11			3800
			AV. = 4130
777-1	Shear at 76° after 7 days immersion in ethylene glycol (AN-E-2)	2000 AV.	4500(control -not)
-2			4410 immersed)
-3			4360
-4			4365
-5			4355
-6			4260
-7			4360
-8			4510
-9			4360
-10			4215
-11			3625
			AV. = 4282

Table 2 Continued - TEST DATA OBTAINED ON PA-101 CEMENT CURED AT 250°F

779-1	Shear at	2000 AV.	4185(Control-not
-2	76°F after		4450 immersed)
-3	7 days		4455
-4	immersion		4550
-5	in hydraulic		4650
-6	oil (AN-O-366)		4600
-7			4610
-8			4450
-9			4450
-10			4445
-11			<u>4350</u>
		AV. =	4501
781-1	Shear at	2000 AV.	3200(Control-not
-2	76°F after		4600 immersed)
-3	7 days		4550
-4	immersion		4450
-5	in hydro-		4350
-6	carbon fluid		4350
-7			4400
-8			4500
-9			4500
-10			4450
-11			<u>3050</u>
		AV. =	3885
773-1	Shear at	2000 AV.	4250(control-not
-2	76°F after		4050 immersed)
-3	30 days		4350
-4	immersion in		4600
-5	water		4500
-6			4600
-7			4700
-8			4950
-9			4850
-10			4700
-11			<u>4050</u>
		AV. =	4535

Table 3

**EFFECT OF SURFACE PREPARATION OF ALUMINUM
ON BOND STRENGTH PA-101 ADHESIVE**

Sample No.	Curing Temperature °F	Cleaning Method	Shear in Adhesive psi at 76°F	Shear in Adhesive psi at 180°F
905-1	300	Sprex AC	4020	
2		alkaline	3870	
3		bath, 10		2250
4		minutes at		2250
5		160°F		2250
906-1	250	Sprex AC	4350	
2		alkaline	4400	
3		bath, 10		2050
4		minutes at		2150
5		160°F		2250
907-1	300	Acetone	3900	
2		Wipe	4000	
3				2200
4				2150
5				2150
908-1	250	Acetone	3675	
2		Wipe	4030	
3				1990
4				2040
5				1940
909-1	300	Soap	3550	
2		and	3850	
3		Water		2000
4				2050
5				2000
910-1	250	Soap	2950	
2		and	3000	
3		Water		1600
4				1350
5				1200
920-1	300	Sprex AC	3950	
2		and	4050	
3		chromic-		2400
4		sulfuric		2350
5		acid		2300
918-1	250	Sprex AC	4200	
2		and	4000	
3		chromic-		2100
4		sulfuric		2150
5		acid		2100

Table 4

INFLUENCE OF NUMBER OF APPLICATION COATS
ON STRENGTH PROPERTIES OF PA-101 CEMENT

Sample No.	Number of Coats	Cured Thickness in in.	Shear in Adhesive psi at 76°F	Shear in Adhesive psi at 180°F
930-1	One	.0025	3580	
12		"	3530	
13	300°	"		1960
14	Cure	"		2060
15		"		2060
931-1	One	.002	3480	
12		"	3630	
13	250°	"		1665
14	Cure	.0025		1765
15		"		1860
917-1	Two	.003	3900	
12		"	3700	
13	300°	"		2100
14	Cure	"		2200
15		"		2150
918-1	Two	.003	4200	
12		"	4000	
13	250°	"		2100
14	Cure	"		2150
15		"		2100
922-1	Three	.0055	4000	
12		"	3970	
13	300°	"		1960
14	Cure	.005		2155
15		.0045		2115
923-1	Three	.006	4350	
12		.0055	4350	
13	250°	.005		1900
14	Cure	"		2000
15		"		1850
924-1	Four	.006	3920	
12		.0055	3970	
13	300°	.0045		1865
14	Cure	.005		1910
15		"		1960

Table 4 Continued - INFLUENCE OF NUMBER OF APPLICATION COATS ON STRENGTH PROPERTIES OF PA-101 CEMENT

Sample No.	Number of Coats	Cured Thickness in in.	Shear in Adhesive psi at 76°F	Shear in Adhesive psi at 180°F
925-1	Four	.0065	3870	
-2		.0055	3970	
-3	250°	.0045		1325
-4	Cure	.005		1470
-5		.0045		1375
926-1	Five	.0065	3725	
-2		.006	3775	
-3	300°	.005		1420
-4	Cure	"		1600
-5		"		1600
927-1	Five	.005	3675	
-2		.0055	3630	
-3	250°	.0045		1275
-4	Cure	.0045		1175
-5		.005		1175
928-1	Six	.0055	3350	
-2		.005	3355	
-3	300°	.0045		1080
-4	Cure	"		1130
-5		"		1030
929-1	Six	.005	3300	
-2		.005	3350	
-3	250°	.0045		950
-4	Cure	.004		1050
-5		.004		1000

Table 5

INFLUENCE OF BONDING PRESSURE ON
SHEAR STRENGTH OF PA-101 CEMENT

Sample No.	Curing Temperature °F	Pressure psi	Shear in Adhesive psi at 76°F	Shear in Adhesive psi at 180°F
903-1	300	50	3250	
12			3350	
13				1815
14				1855
15				1915
904-1	250	50	3000	
12			3250	
13				1550
14				1500
15				1400
827-1	300	100	4000	
12			4000	
13				2100
14				2150
15				2000
828-1	250	100	4200	
12			4200	
13				1900
14				1900
15				1850

Table 6AVERAGE SHEAR STRENGTH TEST DATA ON ALL ADHESIVE FORMULATIONS
OF BUNA N- PHENOLIC RESIN TYPE

Adhesive Designation	Curing Temperature °F	Average Shear Strength psi at:		
		-70°F	+76°F	+180°F
PA-45	300	4195	1560	
PA-46	300	4755	2960	
PA-46	250	4367	2500	
PA-46	200	3170	2140	
PA-47				
PA-48	300		3060	775
PA-49	300		3620	160
PA-49	200		2510	190
PA-50	300	4000	3550	475
PA-50	200		2520	197
PA-51	300	3990	2550	1170
PA-52	300		3600	1065
PA-54	300		2710	1000
PA-54	200		2050	47
PA-55	200		3405	100
PA-56	200		3320	65
PA-57	200		3210	1070
PA-58	200		2100	550
PA-59	200		1275	315
PA-60	200		2211	222
PA-61	200		1420	570
PA-62	200		1455	720
PA-63	200		925	165

Table 6 (con't)

AVERAGE SHEAR STRENGTH TEST DATA ON ALL ADHESIVE FORMULATIONS
OF BUNA N- PHENOLIC RESIN TYPE

Adhesive Designation	Curing Temperature °F	Average Shear Strength psi at:		
		-70°F	+76°F	+180°F
PA-64	200		1225	195
PA-65	200		2800	1350
PA-66	200		2170	665
PA-67	200		2650	930
PA-67	200		850	390
PA-67	300		3820	2700
PA-67	300		3200	1350
PA-68			Very poor	
PA-69	300		3450	2400
PA-69	200		2070	1250
PA-70	300		3620	2745
PA-70	200		2950	1175
PA-71	200		2480	740
PA-72	200		2730	970
PA-74	200		1760	505
PA-74	300		2700	1820
PA-75	200		2450	625
PA-75	300		3600	2300
PA-76	200		3270	1870
PA-76	300		3200	1870
PA-77	200		1520	430
PA-77	300		3550	2020

Table 6 (con't)

AVERAGE SHEAR STRENGTH TEST DATA ON ALL ADHESIVE FORMULATIONS
OF BUNA N- PHENOLIC RESIN TYPE

Adhesive Designation	Curing Temperature °F	Average Shear Strength psi at:		
		-70°F	+76°F	+180°F
PA-78			Very poor	
PA-79	200		2450	670
PA-79	300		1905	1060
PA-80	200		2450	745
PA-80	300		3925	2700
PA-81	200		690	180
PA-81	300		1650	710
PA-82	300		2400	1405
PA-82	200		2400	425
PA-83	300		2830	1720
PA-83	200		3300	525
PA-84	300		2030	570
PA-84	200		585	250
PA-85	300		2900	1700
PA-85	200		2870	610
PA-86	Very poor			
PA-87	300		2770	1980
PA-87	200		2220	560
PA-88	300		3440	2180
PA-88	200		2130	690
PA-89	300		3170	1720
PA-89	200		1625	480

Table 6 (con't)

AVERAGE SHEAR STRENGTH TEST DATA ON ALL ADHESIVE FORMULATIONS
OF BUNA N- PHENOLIC RESIN TYPE

Adhesive Designation	Curing Temperature °F	Average Shear Strength psi at:		
		-70°F	+76°F	+180°F
PA-90	300		2630	1920
PA-90	200		2340	175
PA-91	300		2275	850
PA-91	200		1200	255
PA-92	300		1500	440
PA-92	200		Failed in machining	
PA-93	300		3720	1700
PA-93	200		1200	305
PA-94	300		3160	1610
PA-94	200		1515	445
PA-95	300		3000	2460
PA-95	200		1410	395
PA-96	300		1850	715
PA-96	200		680	92
PA-97	300		2370	970
PA-97	200		500	200
PA-98	300		3430	1480
PA-98	200		2460	480
PA-99	300		3775	1820
PA-99	200		3106	700
PA-100	300		3640	2060
PA-100	200		2800	870

Table 6 (Con't)

**AVERAGE SHEAR STRENGTH TEST DATA ON ALL ADHESIVE FORMULATIONS
OF BUNA N- PHENOLIC RESIN TYPE**

Adhesive Designation	Curing Temperature °F	Average Shear Strength psi at:		
		-70°F	+76°F	+180°F
PA-101	300	5250	4325	2500
PA-101	200		3500	1050
PA-101	250	4975	4230	2010
PA-102	300		2590	1335
PA-102	250		2200	740
PA-103	300		3805	2200
PA-103	250		3825	1830
PA-104	300		3975	1960
PA-104	250		3200	1420
PA-105	300		3815	2120
PA-105	250		4010	1370
PA-106	300		3725	1380
PA-106	250		2775	900
PA-107	300		3975	2390
PA-107	250		4050	2240
PA-108	300		3825	1860
PA-108	250		3875	1545

Table 7

ADHESIVE FORMULATIONS - PA-1 THROUGH PA-10

Formula No.	PA-1	PA-2	PA-3	PA-4	PA-5	PA-6	PA-7	PA-8	PA-9	PA-10
Hycar PA-21	50	50	50	50	50	50	50	50	50	50
Bakelite BR 3360	50									
Durez 12687		50								
Durez 590			50							
Durez 7031-A				50						
Bakelite RD-4933					50					
Synvar RC 50 D						50				
Epon 1007							50			
Vinyl chloride acetate								50		
Elvaset 41 A 95									50	
Vinyl acetate AYAF										50

Table 8

ADHESIVE FORMULATIONS - PA-11 THROUGH PA-18

Formula No.	PA-11	PA-12	PA-13	PA-14	PA-15	PA-16	PA-17	PA-18
Hycar PA-21	50	50	50	50	50	50	50	50
Durez 10390	50							
Synvar RC 50 D plus 10% hexa		50						
Durez 175			50					
Durez 14574				50				
Durez 11078					50			
Marbon 8000						50		
Bakelite BR 15401							50	
Durez 10303								50

Table 9

ADHESIVE FORMULATIONS -- PA-19 through PA-34

Formuls No.	PA-19	PA-20	PA-21	PA-25	PA-26	PA-27	PA-28	PA-30	PA-31	PA-32	PA-34
Hycar PA-21	100	100	100	100	100	100	100	100	100	100	100
SRF Carbon Black	50	50	50	50	50	50	50	50	50	50	50
Sulfur	4	4	4	8	8	8	4	4	4	4	4
Trimene Base	4	4	4	4	4	4			4		4
Durez 12687	100			100			100				
Durez 7031-A		100			100						
Bakelite RD-49-33			100			100					
Bakelite 18791								100	100		
Bakelite 18773										100	
Bakelite 50-63											100

Table 10

ADHESIVE FORMULATIONS - PA-37 through PA-47

Formula No.	PA-37	PA-38	PA-39	PA-40	PA-41	PA-42	PA-43	PA-44	PA-45	PA-46	PA-47
Hycar PA-21	100	100	100	100	100	50	50	100			50
SRF Carbon Black	50	50	50	50	50	50	50	50		50	
Sulfur	4	4	4	4	4	4	4	4		4	
Trimene Base	4	4									
Durez 12687				50			50		50	50	50
Durez 7031-A			100								
Bakelite RD-49-33			50	100	100	100	50	100	50	50	50
Bakelite 18791											
Bakelite 18773											
Bakelite 50-63											
Bakelite 18306	100										
Bakelite 18661		100									
Plasticizer TP-90-B				10				30			
Hycar CR-25 ST					50	50	100	100	100	50	

Table 11

NITRILE RUBBER-PHENOLIC RESIN ADHESIVE FORMULATIONS
PA-48 THROUGH PA-55

Formula No.	48	48A	48B	49	50	51	52	53	54	55
Hycar CR25ST	100	100	100	100	100	100	100	100	100	100
Carbon Black SRF	50	50	50	50	50	50	75	50	50	75
Zinc Oxide				5	5				5	
Sulfur	4	4	4		0.5	4	4	4	4	4
Stearic Acid										
Diatomaceous Earth				2	2				2	
Bakelite RD-49-33	50	50	75	75	75	50	50	50		50
Durez 12687	50	50	75	75	75	50	50	50		50
Captax		1		1	1					
Tuads				3	2					
Agerite Resin D				2	2				2	
Silene EF						10				
Durez 7031-A										150

Table 12

NITRILE RUBBER-PHENOLIC RESIN ADHESIVE FORMULATIONS
PA-56 THROUGH PA-66

Formula No.	56	57	58	59	60	61	62	63	64	65	66
Hycar OR25 ST	100	100	100	100	100	100	100	100	100	100	100
Carbon Black SRF	50	50	50	50	50	50	50	50	50	50	50
Zinc Oxide		5	5	5	5	5	5	5	5	5	5
Sulfur	8	3	3	3	3	3	3	3	3	3	3
Stearic Acid		1	1	1	1	1	1	1	1	1	1
Diatomaceous Earth											
Bakelite RD-49-33	50	50	50	50	50	50	45	50	50	50	50
Durez 12687	50	50	50	50	50	50	45	50	50	50	50
Captax		2	2	2	1	1	2	1	1	2	2
TUADS											
Agerite Resin D		1	1	1	1	1	1	1	1	1	
Butyl Eight		7			7	7	7	7		7	7
Hexamethylenetetramine				5							
Methyl Zimate				.1	.1	.1		1.1	1.1		
Bakelite BR-7							8				
Paraformaldehyde							2				
Butyl Zimate											1.1

Table 13

NITRILE RUBBER - PHENOLIC RESIN ADHESIVE FORMULATIONS
PA -57 THROUGH PA-75

Formula No.	PA-57	PA-68	PA-69	PA-70	PA-71	PA-72	PA-73	PA-74	PA-75
Hycar OR-25ST	100	100	100	100	100	100	100	100	100
Carbon Black SRF	50	50	50	50	50	50	50		75
Carbon Black HMF								50	
Sulfur	3	3	3	3	3	3	3	3	3
Stearic Acid	1	1	1	1	1	1	1	1	1
Zinc Oxide	5	5	5	5	5	5	5	5	5
Agerite Resin D	1	1	1	1	1	1	1	1	1
Captax	2	2	2	2	2	2	2	2	2
Butyl Eight	7	7	7	7	7	7	7	7	7
Durez 7031-A	50	50	50	50	75	150		50	50
Bakelite 18773	50	50	50	50	75		50	50	50
Durez 12687									
Nitropropane		100							
Boron Fluoride									
Phenol Complex BF ₃				2					
Parlon 125 cps									

Table 14

NITRILE RUBBER - PHENOLIC RESIN ADHESIVE FORMULATIONS
PA-76 THROUGH PA-85

Formula No.	PA-76	PA-77	PA-78	PA-79	PA-80	PA-81	PA-82	PA-83	PA-84	PA-85
Hycar CR-25ST	100	100	100	100	100	100	100	100	100	90
Carbon Black SRF	50	50	50	50	50	50	50	50	50	50
Sulfur	3	3	3	3	3	3	3	3	3	3
Stearic Acid	1	1	1	1	1	1	1	1	1	1
Zinc Oxide	5	5	5	5	5	5	5	5	5	5
Agerite Resin D	1	1	1	1	1	1	1	1	1	1
Captax	2	2	2	2	2	2	2	2	2	2
Butyl Eight	7	7		7	7	7	7	7	7	7
Durez 7051-A	50	50	50	50	50	50	50	50		100
Bakelite 18773	50	50	50	50	50	50	50	50	100	
Mica	20									
Litharge			2							
Boron Fluoride				2						
Ammonia Complex										
Chemigum N3NS										

Table 15

NITRILE RUBBER -- PHENOLIC RESIN ADHESIVE FORMULATIONS
PA-36 THROUGH PA-94

Formula No.	PA-86	PA-87	PA-88	PA-89	PA-90	PA-91	PA-92	PA-93	PA-94
Hycar OR-25ST	100	100	100	100	100	100	100	100	100
Carbon Black SRF	50		50	50	50			50	
Sulfur	3	3	3	3	3	3	3	3	3
Stearic Acid	1	1	1	1	1	1	1	1	1
Zinc Oxide	5	5	5	5	5	5	5	5	5
Agerite Resin D	1	1	1	1	1	1	1	1	1
Captax	2	2	2	2	2	2	2	2	2
Butyl Eight	7	7	7	7	7	7	7	7	7
Varcum 5138	100								
Carbon Black EPC		50							
Durez 7031-A		100	50				50		50
Durez 12687			50						
Durez 10128 plus hexa				50	100	53.7		54	
Bakelite 18773									
Alcoa Powder R-20				50		46.3	50	50	50
Iron Oxide No. 507							50		50

Table 16

NITRILE RUBBER - PHENOLIC RESIN ADHESIVE FORMULATIONS
PA-95 THROUGH PA-100

Formula No.	PA-95	PA-96	PA-97	PA-98	PA-99	PA-100	
						Part 1	Part 2
Hycar CR-25ST			100	100	100	100	
Hycar CR-15EP	100	100					
Carbon Black SRF	20	20	50	50	50		
Sulfur	3	3	3	3	3		3
Stearic Acid	1	1	1	1	1		1
Zinc Oxide	5	5	5	5	5		5
Agerite Resin D	1	1	1	1	1		1
Captax	2	2	2	2	2		2
Butyl Eight	7	7	7	7	7		7
Durez 7031-A	50	50	50	50		50	
Bakelite 18773	50	50	50			50	
Bakelite 18773 Partially cured				50	50		
Durez 7031-A Partially cured							50

Table 17

NITRILE RUBBER - PHENOLIC RESIN ADHESIVE FORMULATIONS
PA-101 THROUGH PA-108

Formula No.	PA-101 Part 1 & 2	PA-102 Part 1 & 2	PA-104 Part 1 & 2	PA-105 Part 1 & 2	PA-106 Part 1 & 2	PA-107 Part 1 & 2	PA-108 Part 1 & 2
Hycar CR 25ST	100	100	100	100	100	100	100
Carbon Black SRF	50	50	50	50	50	50	50
Sulfur	3	1 3	3	3	3	3	3
Stearic Acid	1		1	1	1	1	1
Zinc Oxide	5	5	5	5	5	5	5
Agerite Resin D	1	1	5	1	1	1	1
Captax	2	2	2	2	9	9	2
Butyl Eight	7		7	7			7
Bakelite 18773	50	50	50	50	50	50	50
Durez 7031 A	50	50	50	50	50	100	100

Table 18

INDEX TO MATERIALS USED IN ADHESIVE FORMULATIONS

<u>Material Designation</u>	<u>Type</u>	<u>Manufacturer</u>
Agerite Resin D	Rubber antioxidant	Vanderbilt Co., Inc. 230 Park Ave. New York 17, N.Y.
Alcoa Powder R-20	Aluminum oxide filler	The Aluminum Company of America Chemicals Div. Pittsburgh, Penna.
Bakelite RD-49-33	Thermosetting phenolic resin	Bakelite Corp. 30 East 42nd St. New York 17, N.Y.
Bakelite 18791	Thermosetting phenolic resin	Bakelite Corp. 30 East 42nd St. New York 17, N.Y.
Bakelite 18773	Thermosetting phenolic resin	Bakelite Corp. 30 East 42nd St. New York 17, N.Y.
Bakelite 50-63	Thermosetting phenolic resin	Bakelite Corp. 30 East 42nd St. New York 17, N.Y.
Bakelite 18306	Thermosetting phenolic resin	Bakelite Corp. 30 East 42nd St. New York 17, New York
Bakelite 18661	Thermosetting phenolic resin	Bakelite Corp. 30 East 42nd St. New York 17, New York
Bakelite BR-7 Bakelite 3360	Resorcinol resin thermoplastic resin	Bakelite Corp. 30 East 42nd St. New York 17, New York
Boron Fluoride Phenol Complex BF_3	Catalyst	Allied Chemical & Dye Corp. General Chemical Division Claymont Development Lab. Marcus Hook, Penna.
Boron Fluoride Ammonia Complex	Catalyst	Allied Chemical & Dye Corp. General Chemical Division Claymont Development Lab. Marcus Hook, Penna.

Table 18 (con't)

INDEX TO MATERIALS USED IN ADHESIVE FORMULATIONS

<u>Material Designation</u>	<u>Type</u>	<u>Manufacturer</u>
Butyl Eight	Rubber accelerator	Vanderbilt Co. Inc. 230 Park Ave. New York 17, N.Y.
Butyl Zimate	Accelerator for vulcanizing rubber	Vanderbilt Co. Inc. 230 Park Ave. New York 17, N.Y.
Carbon Black SRF	Rubber reinforcer-filler	Binney & Smith Co. P.O. Box 431 Easton, Penna.
Carbon Black EPC	Rubber reinforcer-filler	Binney & Smith Co. P. O. Box 431 Easton, Penna.
Carbon Black HMF	Rubber reinforcer-filler	Binney & Smith Co. P.O. Box 431 Easton, Penna.
Captax	Rubber Accelerator curing agent	Vanderbilt Co., Inc. 230 Park Ave. New York 17, N.Y.
Chemigum N3NS	Nitrile type synthetic rubber	Goodyear Tire & Rubber Co. Chemical Division Akron 16, Ohio
Durez 12687	Thermosetting phenolic resin	Durez Plastics and Chemical Corp. - Walck Road North Tonawanda, N.Y.
Durez 7031-A	Thermosetting phenolic resin	Durez Plastics and Chemical Corp. - Walck Road North Tonawanda, N.Y.
Durez 10128	Thermosetting phenolic resin	Durez Plastics and Chemical Corp. - Walck Road North Tonawanda, N.Y.
Durez 590	Thermoplastic resin	Durez Plastics and Chemical
Diatomaceous Earth	Filler	Johns-Manville 22 East 40th St. New York 16, N.Y.
Epon 1007	Epoxy type resin	Shell Chemical Corp. 500 Fifth Ave. New York 18, N.Y.
Hycar OR-15-EP	Nitrile type synthetic rubber	B. F. Goodrich Chemical Co. Rose Building Cleveland 15, Ohio
WADC TR 52-156	31	

Table 18 (con't.)

INDEX TO MATERIALS USED IN ADHESIVE FORMULATIONS

<u>Material Designation</u>	<u>Type</u>	<u>Manufacturer</u>
Hycar CR-25ST	Nitrile type synthetic rubber	B. F. Goodrich Chemical Co. Rose Building Cleveland 15, Ohio
Hycar PA-21	Polyacrylic type synthetic rubber	B. F. Goodrich Chemical Co. Rose Building Cleveland 15, Ohio
Hexamethylene titramine	Curing agent for phenolic resins	E. I. Du Pont De Nemours & Co., Inc. Wilmington 98, Delaware
Iron Oxide No. 507	Filler	Chas. A. Wagner Co. 813 Callowhill St. Philadelphia 23, Penna.
Litharge	Milcanizing agent for rubber	E. I. Du Pont De Nemours & Co., Inc. Wilmington 98, Delaware
Methyl Zimate	Accelerator for vulcanizing rubber	Vanderbilt Co., Inc. 230 Park Ave. New York 17, N.Y.
Mica	Filler	The Micalith Corp. York, Penna.
Nitropropane	Anti-gilling agent	Commercial Solvents Corp. 17 East 42nd St. New York 17, New York
Paraformal dehyde	Curing agent	E. I. Du Pont De Nemours & Co., Inc. Wilmington 98, Delaware
Parlon 125 cps	Rubber derivative resin	Hercules Powder Co. Wilmington, Delaware
Silene EF	Filler	Pittsburgh Plate Glass Co. Columbia Chemicals Div. Fifth Ave. & Bellefield Pittsburgh 13, Penna.
Stearic Acid	Activator for zinc oxide in curing rubber	W. C. Hardesty Co. 41 East 42nd St. New York 17, New York

Table 18 (con't.)

INDEX TO MATERIALS USED IN ADHESIVE FORMULATIONS

<u>Material Designation</u>	<u>Type</u>	<u>Manufacturer</u>
Sulfur	Vulcanizing agent for rubber	E. I. Du Pont De Nemours & Co., Inc. Wilmington 98, Delaware
Synvar RC-50-D	Thermosetting phenolic resin	Synvar Corp. Wilmington, Delaware
Tuads	Accelerator for vulcanizing rubber	Vanderbilt Co., Inc. 230 Park Ave. New York 17, New York
Trimene Base	Catalyst for cure of polyacrylic rubber	Naugatuck Chemical Co. 1230 Ave. of the Americas New York 20, New York
Varcum 5138	Thermoplastic resin	Varcum Chemical Corp. Niagara Falls, New York
Zinc Oxide	Vulcanizing agent for rubber	American Firstoline Corp. 420 Lexington Ave. New York 17, New York