TRACOR Project No. 074-003
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INVESTIGATION OF ADDITIVES FOR IMPROVEMENT of ADHESIVE AND ELASTOMER PERFORMANCE

FINAL REPORT

Contract No. NAS8-24073
George C. Marshall Space Flight Center
National Aeronautics and Space Administration

July 13, 1970

TRACOR

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ABSTRACT

A two-task program was completed which resulted in an evaluation of several coupling agents in adhesive-substrate and elastomer-filler systems. This was undertaken in an effort to gain more understanding of the behavior of these adhesion promoters and to provide practical data on beneficial systems over a wide temperature range.

The first task was a literature survey which provided a comprehensive background on the various approaches to adhesion promoters. Over 1000 references dated from 1950 to July, 1969, were collected and catagorized; and more than 120 commercial firms were contacted for data on their products. This information resulted in a comprehensive review article which is attached to this report as an appendix. This compilation covers the three principal agent types, silane, chromium complex and phosphorus ester, as well as several miscellaneous materials.

The second task was an experimental one which involved testing a total of 19 different agents in urethane and epoxy adhesives and in a urethane elastomer. For adhesive substrates, in lap shear tests, aluminum, mild steel, stainless steel and glass cloth on aluminum carrier were utilized. For T-peel only aluminum was used with urethane adhesive. Alumina and fumed silica were incorporated as filler in the elastomer.

The test method involved first establishing an optimum, reproducible baseline value for each system at -320, +75 and +200°F. Then each additive was screened at 1% concentration at 75°F. From these data the few agents which showed significant benefit were tested further at room temperature by varying the concentration of each. Then, when the optimum concentration

was determined, the system was subjected to testing at -320 and +200°F.

To summarize the lap shear results, several agents were beneficial over the temperature range in the urethane adhesive on all substrates except glass cloth. More agents were effective on aluminum than on mild or stainless steel. Improvements of 50-100% are possible for the urethane when additives are incorporated.

For the epoxy adhesive fewer agents were effective, and the improvements noted were less significant, more on the order of 10-40% with infrequent excursions to ~70%. It is noteworthy that in many cases the additives actually were harmful at low and high temperatures.

It is postulated that the decrease in strength of epoxy noted at +200°F with additives is due to the lowering of the glass transition temperature (Tg) of the bulk adhesive. A graph of shear strength at +200°F vs Tg of various adhesive composition showed a linear relationship and thus tends to confirm the theory

No additives were found which would improve adhesion of epoxy to glass cloth when tested in a lap shear bond line between aluminum coupons.

A few agents were beneficial in T-peel tests of urethane/aluminum but only at +200 and 75°F and not at -320°F, probably due to increase of bulk modulus of the urethane at low temperatures.

With urethane as an elastomer, two fillters (silica and alumina) were used with three atents. In no case was a beneficial effect noted on the tensile strength of the elastomer. The elongation to break was increased somewhat however.

For low temperature (-320°F) testing a special cryogenic chamber was designed to hold liquid nitrogen and to fit on the lower jaw of the Instron. This system permitted testing of lap shear specimens while immersed in liquid nitrogen.

It is to be noted that this work is not a criticism or endorsement of any product or material tested since the conditions to which they were subjected constitute a special use.

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1. PROGRAM OBJECTIVES AND APPROACH

The objectives of this investigation were to derive a basic understanding of the behavior of coupling agents and to provide practical data over a wide range of temperatures. Considerable data were available at the start of this program on theories of adhesion, coupling agents, and their mechanisms. However, most of it dealt with the application of the agent to the substrate prior to adhesive bonding and primarily with glass substrates. A cursory investigation* showed that incorporation of the agent into the adhesive mixture was a useful approach to improving bond strength. Further, it demonstrated the benefits of using such a system on metal substrates.

The investigation reported herein was designed to comprehensively study the utility of incorporating adhesion promoters into the uncured resin. This means that different adhesives, substrates and agents needed to be screened. Further, the beneficial effects of these materials at cryogenic (-320°F) and high (+200°F) temperatures were important.

The program was divided into two tasks: Literature and Experimental. The first was composed of three phases, data collection, data analysis, and review preparation. This was to precede all experimental work so that proper agents could be chosen and previous work would not be duplicated. The review article resulting from Task I was to be a comprehensive study of all agent types (silanes, phosphorus compounds and chromic acid complexes).

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*L. M. Thompson and W. E. Hill, NASA Technical Memorandum NASA TM-X-53676, George C. Marshall Space Flight Center, Huntsville, Alabama.

The second task was the experimental evaluation of all systems. At the start of this task 19 agents were selected to be tested in epoxy and urethane adhesives on aluminum, mild steel, stainless steel and glass substrates. After an initial screening at room temperature the best materials were scheduled for comprehensive testing at extreme temperatures.

Other tests to be run to screen these agents were T-peel and mechanical tests on filled-elastomers. This was included to determine the effect of agents on other than lap shear tests and on their ability to couple fillers to bulk resins.

The following sections are divided into Experimental Procedure, Results and Discussion--Task I and Task II, Summary and Conclusions, Acknowledgements, and finally the review article is included as an Appendix.

2. EXPERIMENTAL PROCEDURE

2.1 Adhesives

Two adhesives were selected for use throughout the experimental program. Adiprene L-100* was chosen as a urethane system; the process used for it was to mix the resin at room temperature with the coupling agent and 0.2 wt-% glass beads (2.4-3.5 mil**), add 12.5 wt-% melted MOCA* at 121°C with careful mixing, apply to the substrate, cure at room temperature in the mold under pressure for 16-24 hours, then cure at 160°F for 24 hours, and test within 6 hours after any necessary flash removal.

For the epoxy system, EPON VIII*** was mixed with 0.2 wt-% glass beads and 6 wt-% Curing Agent "A,"*** then applied to the substrate and cured for 90 minutes at 93°C (200°F).

2.2 Substrates

Preparation of the bonding surfaces was well defined and controlled throughout the test program. It should be noted that considerable effort was expended optimizing these treatments for the maximum and most reproducible bond strengths. This is a most important part of a program such as this. For aluminum this process constituted wiping with trichloroethylene, vapor degreasing with the same for 10 minutes, etching for 20 minutes in a bath at 66°C (composition: 65.4 wt-% water, 29.9 wt-% H_2SO_4,

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*E. I. duPont de Nemours and Company

**Microbeads Division of Cataphote Corporation. A calculation has shown that the total surface area of the glass is far less than that of the actual bond, so agent/glass interaction is minimal.

***Shell Chemical Company

and 7.7 wt-% sodium dichromate dihydrate), washing with tap water, then with distilled water, drying at 66°C for 10 minutes, and storing in a desiccator until use. For controlling reproducibility it was very important to use fresh etchant for the aluminum substrates; therefore, 2.5 liters of solution were used for 64 lap shear coupons or two T-peel panels and then discarded.

The mild steel substrates were wiped and vapor degreased with trichloroethylene, sanded with #180 grit paper, degreased a second time and used immediately.

Stainless steel specimens were degreased with trichloroethylene, cleaned for 10 minutes at 75°C (cleaning solution: 3 parts sodium metasilicate, 1.5 parts sodium hydroxide, 0.5 parts Alconox, and 138 parts distilled water), etched in concentrated hydrochloric acid for 10 minutes at room temperature, rinsed in distilled water, oven dried, and used immediately.

The glass cloth used after the initial cloth screening was #116. The VOLAN finish was removed by heating the cloth at 450°C for 24 hours. The glass cloth was then wiped and vapor degreased with trichloroethylene for 20 minutes prior to bonding.

2.3 Elastomers

The material used for all elastomer tests was Adiprene L-100/MOCA in the same mixing ratio as in the urethane/lap shear tests. The procedure for molding the elastomers is outlined below:

(1) The Adiprene L-100 was degassed at room temperature.

(2) The Adiprene L-100 (containing filler and/or agent when applicable) was heated to 100°C before being mixed with melted MOCA.

(3) The mold was heated to about 100°C before the hot mixture was carefully poured into it.

(4) The few bubbles that formed were carefully removed with a small, pointed knife.

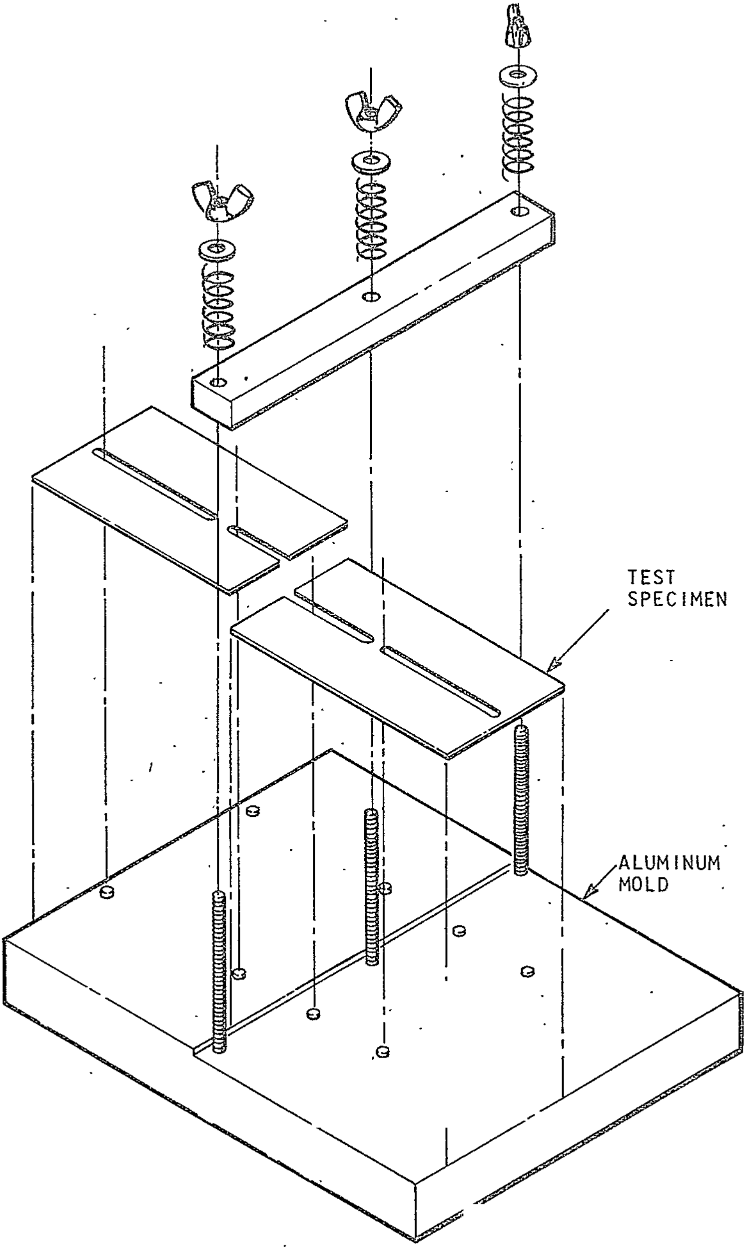
(5) The cure schedule for the urethane consisted of 16-24 hours at room temperature and 24 hours at 71°C.

The elastomer mold was an 8" square aluminum dish about ¼" deep. This size allowed about 8 dumbbell tensile specimens to be cut from each sheet of elastomer.

2.4 Test Methods and Specimens

2.4.1 General Preparation and Tensile Testing - The method for molding lap shear coupons is shown in Figure 1. The lower two-finger pieces were covered with adhesive over the ½" faying surface and fitted into the guide pins on the lower step of the mold. Adhesive was also applied to the upper bonding piece, and it was laid over the first one to fit the pins on the higher step. Then the bar, springs, washers, and wing-nuts were applied to maintain equal pressure during cure. On removal from the mold, the double fingers were sawed to give two lap shear specimens or four per mold.

The lap shear coupons were tested in tension on an Instron tester at a crosshead speed of 0.05 inches/minute or



LAP SHEAR TEST SPECIMEN MOLD

FIGURE 1

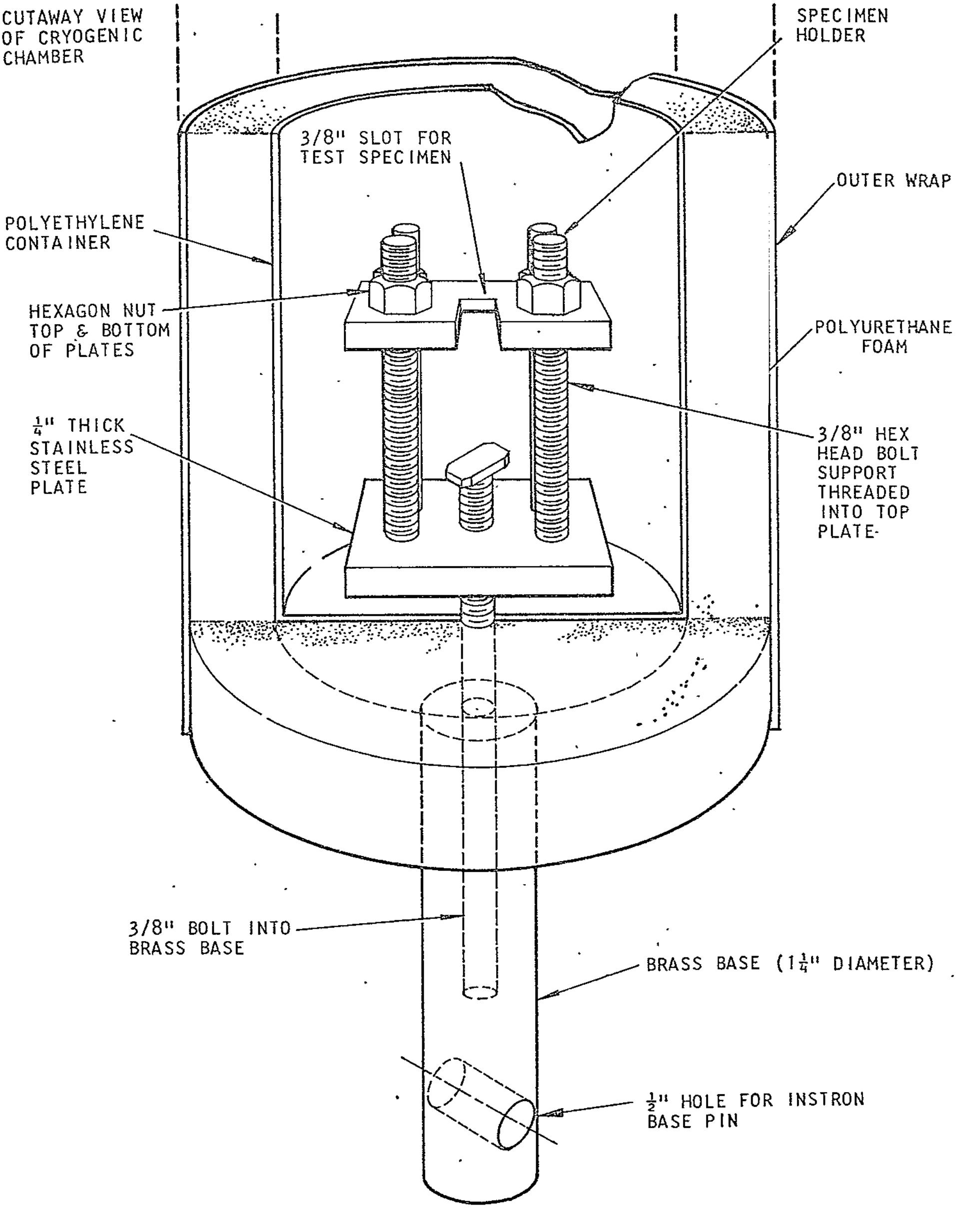
A6-191-36
5/4/70 JOHNSON (KN)

approximately 1400 psi/minute according to the procedure outlined in ASTM-D-1877-61T. After failure the bondlines were examined for degree of cohesive or adhesive failure.

T-peel specimens were bonded as 9" x 12" panels and then cut into 1" x 12" strips after cure. The substrate used was 0.020" 2024-T3 aluminum. Three inches on the end of each panel remained unbonded so that the strips could be bent apart to fit into the Instron jaws. The pulling rate of the Instron for T-peel tests was 10 inches/minute as suggested in ASTM-D-1876-61T.

For elastomer testing ASTM-D-412-66 was followed closely. The Instron pulling rate was 20 inches/minute, and an extensometer was fitted to each specimen to facilitate percent elongation measurement.

2.4.2 Extreme Temperature Testing - While all the high temperature (200°F) tests could be run in the Instron environmental chamber, a special chamber was necessary for cryogenic (-320°F) tests to allow rapid and accurate results. Figure 2 is a representation of this device which constitutes a tall polyethylene or thin steel cup insulated with about one inch of polyurethane foam. Through the bottom is projected a bolt which fastens to the lower jaw of the Instron. Fastened to the bolt within the cup is a stainless steel plate which holds the sample in tension. To adapt samples to this particular sample holder, one end of the specimen was fitted with doublers (using the same adhesive as the test), and a hole and bolt were placed through these. This arrangement allowed facile placement of samples into the liquid nitrogen which promoted rapid cooling and provided excellent temperature control. On fracture of the bond, the lower piece was removed from the chamber and another test specimen inserted and readied for test in a short time.



CRYOGENIC CHAMBER

FIGURE 2

2.5 Control Values for Baselines

At the beginning of the experimental portion of the contract (Task II), all systems with no additives were tested to provide reproducible and optimum values. The aforementioned procedures for sample preparation were carefully followed to give maximum and readily reproducible strengths throughout the program. Periodic checks were made to ensure the control values. Table 1 shows the baseline values obtained for each system used.

2.6 Coupling Agents

An extensive review was made of the literature to reveal the types of agents available; that review is presented in this report as Appendix "A." Listed in Table 2 are the nineteen commercially available coupling agents chosen for screening as a result of that review. The materials given in Table 2 with their trade name, manufacturer and chemical identity (if known) were selected on the basis of their chemical structure to eliminate duplication of effort and to establish a relationship between structure and behavior. It should be well understood that it was not the purpose of this work to completely evaluate these agents. The results herein relate to a special use of these materials and are not an endorsement or criticism of any product or manufacturer. Furthermore, as the purpose of this investigation was, in part, to relate behavior to chemical structure, a concentrated effort was made to ascertain from each manufacturer the exact composition of his product.

The general approach to testing was to test each agent at a 1% concentration in the resin. Each additive which demonstrated significant increase over the baseline control value at room temperature was tested further. First it was used at

TABLE 1

BASELINE (CONTROL) SHEAR STRENGTH VALUES FOR ALL ADHESIVE SYSTEMS TESTED (psi)

	-320°F	+75°F	-200°F
Urethane			
Aluminum	5023	1525	545
Mild Steel	4913	988	878
Stainless Steel	4388	1130	510
Glass	--	1400	--
Epoxy			
Aluminum	1562	3150	2621
Mild Steel	1042	2240	1382
Stainless Steel	1610	3631	2570
Glass	--	2967	--

TABLE 2

COMMERCIALLY AVAILABLE COUPLING AGENTS USED AS ADDITIVES IN ADIPRENE L-100 ADHESIVE AND EPON VIII EPOXY

Designation Number or Name	Supplier	Chemical Nomenclature or Description
SWS-401	Stauffer-Wacker Silicone Corp.	A solvent-dispersed metallo-organic bonding agent
SWS-403	Stauffer-Wacker Silicone Corp.	A solvent-dispersed metallo-organic bonding agent
SWS-441	Stauffer-Wacker Silicone Corp.	Dimethyldichlorosilane
SWS-442	Stauffer-Wacker Silicone Corp.	Methyltrichlorosilane
Z-6020	Dow Corning Corp.	N-β-(Aminoethyl)-γ-aminopropyltrimethoxysilane
Z-6040	Dow Corning Corp.	γ-Glycidoxypropyltrimethoxysilane
Z-6076	Dow Corning Corp.	γ-Chloropropyltrimethoxysilane
XZ-8-5059	Dow Corning Corp.	A hydroxy functional silane
XZ-8-5062	Dow Corning Corp.	A hydroxy functional silane
A-151	Union Carbide Corp.	Vinyltriethoxysilane
A-153	Union Carbide Corp.	Phenyltriethoxysilane
A-174	Union Carbide Corp.	γ-Methacryloxy-propyltrimethoxysilane
A-186	Union Carbide Corp.	β-(3,4-Epoxycyclohexyl)-ethyltrimethoxysilane
A-189	Union Carbide Corp.	γ-Mercaptopropyltrimethoxysilane
VOLAN	E. I. duPont de Nemours & Co.	Methacrylato chromic chloride in 2-propanol
SS-4004	General Electric	A silicone primer
WESLINK E	Weston Chemical Co., Inc.	A tri-functional phosphorus ester
CHA		Cyclohexylamine
4-Ampip		4-Aminomethylpiperidine

varying concentrations (1, 3, 5, 10, 15 and occasionally 20 and 25% by weight). From this the optimum concentration was determined, and this level of agent in the adhesive was used for the comprehensive testing.

2.7 Thermal Analysis Procedure

The differential thermal analyses (DTA) performed during the course of this program were performed on the following Robert L. Stone equipment: an SH-11BR2-Al (aluminum) sample holder, an F-1DF furnace, a DTA Furnace Platform (Model JP-202), and a Stone L-202 Recorder-Controller. The SH-11BR2-Al sample holder consisted of two Platinel II ring differential thermocouples and a Chromel-Alumel reference thermocouple. The Platinel II ring differential thermocouples proved to be highly sensitive, and in conjunction with the aluminum sample holder, provided excellent thermal properties with low drift.

The subambient DTA's were performed on a Stone H-5 Subambient connected to the L-202 Recorder-Controller. Liquid nitrogen was used as a coolant, and a temperature range from -150°C to +300°C was explored with this unit. The ring differential thermocouples and the reference thermocouple were iron-constantan.

The samples, ranging in weight from two to six milligrams were contained in small aluminum foil dishes that set on the sample holder rings (the ring differential thermocouples). Alumina, Al_2O_3, was used as a reference because of its inertness over the test temperature range. The sample and reference weights were balanced according to the following formula to effect zero drift:

$$\text{Weight of Reference} = \frac{\text{Weight of Sample} \times \text{Specific Heat of Sample}}{\text{Specific Heat of Reference}}$$

A programmed heating rate of 10°C per minute was maintained throughout the tests as was an amplifier gain setting of 20 μv. All samples were run statically in air. A positive Y-axis deflection indicated an exothermic sample reaction while a negative Y-axis deflection indicated an endothermic sample reaction. This process of thermal analysis permits accurate determination of any phase changes which may occur in any material. That is one may observe crystallinity changes, melting points, decompositions, glass transitions (Tg), etc. The Tg was of particular interest to this program and may be thought of as the point during heating at which the amorphous phase of a polymer goes from a glassy to a rubbery state.

3. RESULTS AND DISCUSSION OF TASK I - LITERATURE SURVEY

3.1 Adhesion and Coupling Agents

Phase I: For a comprehensive data collection, a list of key words was formed and used to search Chemical Abstracts from June, 1969, back through the 1950 volume. This period includes all work pertinent to this problem. The key words were: silanes, coupling agents, adhesion promoters, adhesive additives, chromium complexes, phosphorus esters, Volan, elastomers, fillers, piperidines, silanol, chemisorption, epoxy adhesives, and urethane adhesives. As was expected, a large number of references (over 1100) was discovered, even after an initial elimination conducted during the search. These abstracts were located in Chemical Abstracts, a copy of each was made, and a second analysis was accomplished based on pertinence of the abstracted data. Each remaining abstract was then placed on a Burroughs Unisort Analysis Card to allow it to be categorized for retrieval. On each card the Chemical Abstracts location was also noted.

In addition to the review of the scientific literature, manufacturers' information was sought. Over 120 commercial firms were contacted by letter for the available technical information on their products.

Phase II: A coded system was developed to allow recall of any references containing any particular subject matter, and each card was punched according to the following code:

Adhesive

1. Epoxy
2. Urethane
3. Elastomer
4. Polyester

Adhesive (cont'd.)	5.	Phenolic
	6.	Silicone
	7.	Other
Substrate	11.	Copper
	12.	Aluminum
	13.	Steel
	14.	Glass
	15.	Rubber
	16.	Plastic
	17.	Other
Coupling Agent Type	21.	Phosphorus
	22.	Chromium
	23.	Piperidine
	24.	Silane
	25.	Other
Miscellaneous	31.	Environmental Effects
	32.	Surface Chemistry
	33.	Surface Preparation
	34.	Fillers
	35.	Test Methods

Furthermore, two code positions (not numbered) were used to denote a book or review. Not all the code numbers were used in each category so that there is room for future expansion of the system.

<u>Phase III</u>: Finally, using the above information a review of the available information was written and is attached to this final report as an appendix. This review is a comprehensive summation of published data on adhesion theories and the effects

of various agents and their mechanisms. It is organized into discussions of agents by classes: silanes, chromium complexes, phosphorus compounds, and miscellaneous.

The bibliography attached to the review is broken into two sections: A. pertinent articles on agents, and B. books and reviews which include topics such as adhesion and adhesives. In this bibliography there are included not only the original reference, but the Chemical Abstracts location and a code of the information discussed therein according to the system described above in Phase II.

3.2 Surface Investigation by Infrared Spectroscopy

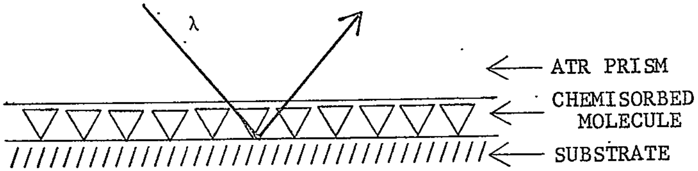
A literature investigation was undertaken to determine the feasibility of using infrared spectroscopy to elucidate the mechanism of chemisorption of coupling agents on various substrates. The results of this survey can be summarized as follows.

A large portion of the work reported on the application of infrared spectroscopy to chemisorption mechanism studies has been done by persons interested in catalysis. The experimental techniques employed and results obtained from such studies, although conceptually related, cannot be directly applied to an adhesion study such as this. The majority of the spectroscopic work reported involves transmission techniques which necessitate a transparent substrate. Several techniques are available for producing such a substrate. The substrate itself may be transparent (e.g., Al_2O_3), the substrate (e.g., a metal) may be supported in a transparent matrix, or the substrate, although not transparent, may be used in thin film form. Unfortunately none of the aforementioned techniques are directly applicable to the study of chemisorption of coupling agents to steel, aluminum or glass.

The results reported do lend confirmation to the fact that, in general, chemisorption of a given species is sensitive to the nature of the substrate surface. Extreme caution must be exercised in extrapolating the data reported for one substrate to a substrate of different chemical composition. In fact, a given substrate will show a pronounced variation in its chemisorption capacity as a function of surface treatment, although it is doubtful that the chemisorption mechanism itself changes.

In recent years much attention has been given to reflection techniques to obtain the infrared spectra of chemisorbed molecules. In general, most of the work reported involves the adsorption of monolayers on either optically transparent substrates or on metallic mirrors. Neither of these techniques is directly applicable to this study. Steel, aluminum and glass are not transparent in the infrared, nor is this study concerned with substrates which have been polished to a mirror finish.

Originally it was thought that attenuated total reflection techniques may be applicable in spite of the opaque nature of the substrate. It was believed that the perturbation of the coupling agent spectrum caused by chemisorption on the substrate could be obtained using the experimental design shown below.



After preliminary experimental work it became obvious that several difficulties would have to be overcome if meaningful spectra were to be obtained. First, there was considerable variation between spectra obtained with a given substrate with different surface finishes. In general "rough" surfaces caused considerable scattering which obscured any fine structure. Second, if a "thick film" of coupling agent, i.e., greater than a few monolayers, was used no perturbation was observed. This is understandable since a perturbation will result only at the site of chemisorption. If nonperturbed groups are present in sufficient numbers, the small perturbation superimposed on the normal absorption will not be observable. Finally, there is some indication that the various ATR prisms (e.g., AgCl, KRS-5, and Si) may present a more "active" substrate to the coupling agent than the substrate in question thus causing a preferential orientation of the coupling agent.

Considering the emphasis of this particular program, the large number and wide chemical variation of the coupling agents under study, the nature of the substrates in question, the results reported in the literature, and the preliminary experimental data available, a comprehensive experimental study of chemisorption of coupling agents via infrared spectroscopy was not justified. However, there is a strong possibility that a detailed, comprehensive study of this type would be invaluable in elucidating the mechanism of chemisorption and in aiding the development of new adhesion promoters.

4. RESULTS AND DISCUSSION OF TASK II - EXPERIMENTAL

4.1 Lap Shear Tests

Each system in this section is subdivided according to adhesive and substrate. The procedure and equipment used for all lap shear tests are given above.

4.1.1 Urethane Testing

4.1.1.1 Urethane/Aluminum System - Table 3 shows the complete results of coupling agent screening with the aluminum/urethane system with an additive concentration of 1.0 wt-%. This shows that five commercial agents contribute to the adhesive strength of urethane on aluminum by the fact that they increase the average adhesive strength by 300 to 625 psi (20 to 40%). These materials (SWS-401, Z-6040, Z-6076, A-186, Weslink E) were thus chosen for comprehensive testing at -320 and 200°F. Also, from these data it is interesting to note that some agents decrease the bond strength of the urethane adhesive significantly. Of course, the amine-terminated additive (Z-6020) was not compatible with the isocyanate resin due to the high reactivity of the two. Of the five final additives selected, one is unknown in composition (SWS-401, an "organometallic"), two are epoxy-terminated methoxysilanes (Z-6040 and A-186), one is a phosphorous ester whose exact structure is unknown (Weslink E), and one is a chloroalkyl methoxysilane (Z-6076). It appears then that the methoxysilane is certainly useable in a urethane system as is an epoxy terminal function.

Table 4 shows the results of concentration variation of the above chosen five coupling agents in the urethane/aluminum system. These data show that a sufficient and optimum concentration

TABLE 3

COUPLING AGENT SCREENING IN THE URETHANE/ALUMINUM SYSTEM

Sample No.	Coupling Agent 1% by wt	High/Low Shear Strength	Average (psi)
517-532	Control	1714/1370	1525
533-540	SWS-401	2600/1428	1881
541-548	SWS-403	1816/1304	1537
677-684	SWS-441	1624/968	1300
685-692	SWS-442	1194/880	1017
N/A	Z-6020	Incompatible	--
565-572	Z-6040	2540/1760	2166
589-596	Z-6076	2368/1424	1905
613-620	XZ-8-5059	1738/1184	1424
597-604	XZ-8-5066	1842/1380	1523
621-628	A-151	1484/1092	1283
629-636	A-153	1552/1170	1385
653-660	A-174	1658/1050	1408

TABLE 3 (CONT'D.)

COUPLING AGENT SCREENING IN THE URETHANE/ALUMINUM SYSTEM

Sample No.	Coupling Agent 1% by wt	High/Low Shear Strength	Average (psi)
661-668	A-186	2040/1430	1802
669-676	A-189	1690/1390	1568
581-588	VOLAN	1740/1408	1571
573-580	SS-4004	1520/1004	1240
605-612	Weslink E	2120/1530	1820
---	4-Ampip	Incompatible	--
1057-1060	CHA	1012/924	977.

TABLE 4

AGENT CONCENTRATION VARIATION IN THE URETHANE/ALUMINUM SYSTEM

Sample No.	Coupling Agent and Concentration	High/Low Shear Strength	Average (psi)
761-764	3% SWS-401	1230/966	1103
765-768	5% SWS-401	1142/1056	1114
769-772	10% SWS-401	834/632	732
773-776	15% SWS-401	1056/926	993
777-780	3% Z-6040	2112/1520	1838
781-784	5% Z-6040	1556/1124	1331
785-788	10% Z-6040	1522/1312	1461
789-792	15% Z-6040	1710/1224	1478
793-796	3% Z-6076	1904/1568	1741
797-800	5% Z-6076	1550/1398	1490
801-804	10% Z-6076	1808/1452	1669
805-808	15% Z-6076	1554/1358	1445

TABLE 4 (CONT'D.)

AGENT CONCENTRATION VARIATION IN THE URETHANE/ALUMINUM SYSTEM

Sample No.	Coupling Agent and Concentration	High/Low Shear Strength	Average (psi)
809-812	3% Weslink E	2080/1710	1875
813-816	5% Weslink E	1418/1100	1304
817-820	10% Weslink E	1536/1054	1346
821-824	15% Weslink E	2110/1230	1578
825-828	3% A-186	2100/1340	1837
829-832	5% A-186	2356/1280	1841
833-836	10% A-186	1766/1296	1477
837-840	15% A-186	1420/1126	1323

for the use of these agents is near 1.0 wt-%, the composition of the agent notwithstanding. As a result, all comprehensive testing with these adhesion promoters was conducted at 1% concentration. The epoxy system, as seen later, behaves somewhat differently.

The results of comprehensive testing of urethane/aluminum at high and low temperature are shown in Table 5. At 200°F where improvement is most important, an increase in strength by nearly 100% results from three agents. At -320°F the results are still quite good for all except SWS-401 which lowers bond strength. This unknown organometallic was one of the poorer performers in this series.

4.1.1.2 Urethane/Mild Steel System - Table 6 shows the results of the coupling agent screening with the mild steel/urethane system with additive concentration of 1.0% by weight. Five (5) commercial agents contribute somewhat to the adhesive strength of urethane on steel; however, only one of the materials (Z-6040) demonstrated a significant benefit. It is interesting that the agents most beneficial in this system were also the only epoxy-terminated compounds tested (Z-6040 and Z-186).

Table 7 shows the effect on adhesion of varying the concentration of Z-6040 from one to fifteen percent in the urethane/steel system. It can be seen that 3% Z-6040 results in the highest shear strength at room temperature. Therefore, this concentration was selected for comprehensive testing, the results of which are shown in Table 8. At 200°F the shear strength was increased by approximately 25% while at -320°F the shear strength was increased by 126% to over 11,000 psi.

4.1.1.3 Urethane/Stainless Steel System - Table 9 shows the effect of coupling agents on the urethane/stainless steel system.

TABLE 5

COMPREHENSIVE TESTING IN THE URETHANE/ALUMINUM SYSTEM

Sample No.	Temp. (°F)	Additive and Concentration	High/Low Shear Strength	Average (psi)
913-920	200	Control	600/484	545
921-928	200	1% SWS-401	824/534	644
929-936	200	1% Z-6040	1348/710	997
997-1004	200	1% Z-6076	1136/982	1062
981-988	200	1% A-186	1058/720	881
965-972	200	1% Weslink E	1154/788	1059
517-732	75	Control	1714/1370	1525
533-540	75	1% SWS-401	2600/1428	1881
565-572	75	1% Z-6040	2540/1760	2166
589-596	75	1% Z-6076	2368/1424	1905
661-668	75	1% A-186	2040/1430	1802
605-612	75	1% Weslink E	2120/1530	1820

TABLE 5 (CONT'D.)

COMPREHENSIVE TESTING IN THE URETHANE/ALUMINUM SYSTEM

Sample No.	Temp. (^{o}F)	Additive and Concentration	High/Low Shear Strength	Average (psi)
953-960	-320	Control	5680/4410	5023
945-952	-320	1% SWS-401	5500/3440	4761
937-944	-320	1% Z-6040	8900/8210	8497
989-996	-320	1% Z-6076	8680/7600	7997
1021-1028	-320	1% A-186	9200/7540	8414
973-980	-320	1% Weslink E	7520/6070	6943

TABLE 6

COUPLING AGENT SCREENING IN THE URETHANE/MILD STEEL SYSTEM

Sample No.	Coupling Agent 1% by wt	High/Low Shear Strength	Average (psi)
217-224	Control	1122/822	988
225-228	SWS-401	1062/854	958
229-232	SWS-403	1180/936	1065
281-284	SWS-441	856/582	732
285-288	SWS-442	662/534	603
---	Z-6020	Incompatible	--
233-236	Z-6040	1676/1332	1545
237-240	Z-6076	1100/924	1049
241-244	XZ-8-5059	926/760	807
245-248	XZ-8-5066	1120/940	991
261-264	A-151	996/830	914
265-268	A-153	1086/868	981
269-272	A-174	1226/796	1010

TABLE 6 (CONT'D.)

COUPLING AGENT SCREENING IN THE URETHANE/MILD STEEL SYSTEM

Sample No.	Coupling Agent 1% by wt	High/Low Shear Strength	Average (psi)
273-276	A-186	1300/824	1096
277-280	A-189	860/800	829
249-252	VOLAN	1030/926	983
253-256	SS-4004	798/700	752
257-260	Weslink E	966/702	847
---	4-Ampip	Incompatible	--
447-450	CHA	949/888	921

TABLE 7

AGENT CONCENTRATION VARIATION IN THE URETHANE/MILD STEEL SYSTEM

Sample No.	Coupling Agent and Concentration	High/Low Shear Strength	Average (psi)
233-236	1% Z-6040	1676/1332	1545
331-334	3% Z-6040	1856/1426	1701
335-338	5% Z-6040	2000/1168	1649
339-342	10% Z-6040	1196/964	1102
343-346	15% Z-6040	1244/732	1100

TABLE 8

COMPREHENSIVE TESTING IN THE URETHANE/MILD STEEL SYSTEM

Sample No.	Temp. (^{o}F)	Additive and Concentration	High/Low Shear Strength	Average (psi)
347-354	200	Control	1046/744	878
355-362	200	3% Z-6040	1270/1012	1074
217-224	75	Control	1122/822	988
331-334	75	3% Z-6040	1856/1426	1701
363-370	-320	Control	5520/4460	4913
371-378	-320	3% Z-6040	11700/10180	11088

TABLE 9

COUPLING AGENT SCREENING IN THE URETHANE/STAINLESS STEEL SYSTEM

Sample No.	Coupling Agent 1% by wt	High/Low Shear Strength	Average (psi)
145S-152S	Control	1316/901	1130
159S-162S	SWS-401	1262/1162	1210
167S-170S	SWS-403	1544/1096	1262
171S-174S	SWS-441	1046/850	994
227S-230S	SWS-442	290/155	222
---	Z-6020	Incompatible	--
191S-194S	Z-6040	1385/1115	1220
219S-222S	Z-6076	1295/1020	1150
183S-186S	XZ-8-5059	720/530	661
187S-190S	XZ-8-5066	1130/922	1040
195S-198S	A-151	1122/720	879
199S-202S	A-153	1045/540	798
203S-206S	A-174	1230/775	1040

TABLE 9 (CONT'D.)

COUPLING AGENT SCREENING IN THE URETHANE/STAINLESS STEEL SYSTEM

Sample No.	Coupling Agent 1% by wt	High/Low Shear Strength	Average (psi)
207S-210S	A-186	1342/1060	1242
211S-214S	A-189	1705/1230	1446
175S-178S	VOLAN	1178/908	1059
215S-218S	SS-4004	1045/980	1012
179S-182S	Weslink E	1020/822	913
---	4-Ampip	Incompatible	--
223S-226S	CHA	850/310	688

Only A-189, a mercapto-functional methoxysilane, and SWS-403 proved to be beneficial in this system, and the agents were selected for concentration variation testing. These data are shown in Table 10.

Since adhesive strengths fell off rapidly when more than 1% of these materials were used, testing was not pursued past the 5% agent level. The results of comprehensively testing these agents at extreme temperatures are given in Table 11. A-189 is the superior performer here increasing strength by ~50% at either extreme temperature.

4.1.1.4 Urethane/Glass Cloth System - For this particular substrate a modified sample preparation was required. A sample of glass cloth was placed in the bondline of a usual lap shear bonding specimen. Of course, in order to obtain valid data, the failure must be adhesive from the glass, so a high urethane-metal bond strength was required. Because of its higher shear strengths in the urethane system, aluminum was chosen as the "carrier" substrate for the glass cloth. Both in baseline determination and agent screening as presented in Table 12, adhesive failure of the urethane from #116 glass cloth occurred. However, in the case of CHA, a combination of adhesive failure from both glass and aluminum substrates occurred.

Only Z-6040, A-186, and A-189 gave any increase at all from the control value, and this difference was so small it was within the experimental error. Therefore, comprehensive testing was not pursued for this system.

To summarize the results of the urethane work, the methoxy functions on silanes appear to present no hindrance to surface bond formation. Further, the mercapto, epoxy, and chloroalkyl functions are generally beneficial as ties with the organic

TABLE 10

AGENT CONCENTRATION VARIATION IN THE URETHANE/STAINLESS STEEL SYSTEM

Sample No.	Coupling Agent and Concentration	High/Low Shear Strength	Average (psi)
263S-266S	3% A-189	1116/924	1045
267S-270S	5% A-189	1270/1060	1131
271S-274S	3% SWS-403	1024/656	886
275S-278S	5% SWS-403	1170/826	968

TABLE 11

COMPREHENSIVE TESTING IN THE URETHANE/STAINLESS STEEL SYSTEM

Sample No.	Temp. (°F)	Additive and Concentration	High/Low Shear Strength	Average (psi)
295S-298S	200	Control	614/414	510
279S-286S	200	1% SWS-403	684/616	650
287S-294S	200	1% A-189	803/702	741
145S-152S	75	Control	1316/901	1130
167S-170S	75	1% SWS-403	1544/1096	1262
211S-214S	75	1% A-189	1705/1230	1446
299S-302S	-320	Control	5400/3900	4388
303S-307S	-320	1% SWS-403	4840/3300	4024
308S-315S	-320	1% A-189	8600/6580	7187

TABLE 12

COUPLING AGENT SCREENING IN THE URETHANE/GLASS CLOTH SYSTEM

Sample No.	Coupling Agent 1% by wt	High/Low Shear Strength	Average (psi)
57G-72G	Control	1600/1184	1400
85G-88G	SWS-401	1146/1020	1100
185G-188G	SWS-403	1444/1204	1323
189G-192G	SWS-441	1276/820	1040
193G-196G	SWS-442	1200/960	1041
---	Z-6020	Incompatible	--
73G-80G	Z-6040	1624/1340	1499
89G-92G	Z-6076	1374/1166	1301
197G-200G	XZ-8-5059	1230/1006	1111
201G-204G	XZ-8-5066	792/658	731
205G-208G	A-151	1320/1232	1265
209G-212G	A-153	1114/948	1017
93G-96G	A-174	1358/1104	1237

TABLE 12 (CONT'D.)

COUPLING AGENT SCREENING IN THE URETHANE/GLASS CLOTH SYSTEM

Sample No.	Coupling Agent 1% by wt	High/Low Shear Strength	Average (psi)
97G-100G	A-186	1372/1152	1497
101G-104G	A-189	1708/1302	1497
213G-216G	VOLAN	1326/1076	1189
217G-220G	SS-4004	1300/732	1071
105G-108G	Weslink E	1340/966	1211
---	4-Ampip	Incompatible	--
81G-84G	CHA	1014/731	865

phase. In contrast, amino functional silanes were harmful to the urethane as were the methylchlorosilanes. Also, vinyl and phenyl substituents on silanes proved detrimental.

4.1.2 Epoxy Testing

4.1.2.1 Epoxy/Aluminum System - Given in Table 13 are the results of the nineteen commercial agents inherently mixed in EPON VIII following the addition of catalyst. Upon investigation of the data, it is seen that the improvement obtained by incorporation of 1% of adhesion promoters in epoxies is small (8% increase in the best case). In this initial screening the most significantly beneficial agents were SS-4004, SWS-401, 4-Ampip, Weslink E, and XZ-8-5062 which were selected for more extensive testing. Unfortunately, the structure of only one of the materials is known with certainty, 4-aminomethylpiperidine, which would be expected to react with the epoxy resin because of its labile primary and/or secondary amine groups.

Previously in this report, it was confirmed that a concentration of 1% of the coupling agent in urethane was near optimum. However, since no data were immediately available concerning the optimum agent concentrations in epoxy systems, a brief study was made. Table 14 gives the data obtained by varying the concentration of those five additives which demonstrate greatest improvement of lap shear adhesive strength in the epoxy/aluminum system. It is obvious that the necessary concentration in the epoxy/aluminum system is not 1% but varies substantially. Weslink E was the only agent tested at 25% concentration since this level was suggested in the manufacturer's literature.

In Table 15 are shown the epoxy/aluminum lap shear strength results at -320 and 200°F using the additives at their optimum concentrations.

TABLE 13

COUPLING AGENT SCREENING IN THE EPOXY/ALUMINUM SYSTEM

Sample No.	Coupling Agent 1% by wt	High/Low Shear Strength	Average (psi)
89-104	Control	3336/2976	3150
317-324 365-388	SWS-401	3484/3204	3303
309-316 361-364	SWS-403	3344/3084	3229
637-644	SWS-441	3340/3120	3212
645-652	SWS-442	3100/2880	2983
169-172	Z-6020	3140/3080	3110
165-168	Z-6040	3270/3140	3205
509-516	Z-6076	3240/2992	3126
501-508	XZ-8-5059	3348/2916	3102
493-500	XZ-8-5066	3472/3036	3293
437-444	A-151	3372/3100	3243
429-436	A-153	3320/3072	3238

TABLE 13 (CONT'D.)

COUPLING AGENT SCREENING IN THE EPOXY/ALUMINUM SYSTEM

Sample No.	Coupling Agent 1% by wt	High/Low Shear Strength	Average (psi)
485-492	A-174	3224/3080	3183
445-452	A-186	3200/3044	3118
421-428	A-189	3360/3036	3209
409-420	VOLAN	3304/3128	3291
549-556	SS-4004	3388/3188	3291
557-564	Weslink E	3492/3244	3392
961-964	4-Ampip	3140/2844	2995
953-956	CHA	3232/3140	3198

TABLE 14

AGENT CONCENTRATION VARIATION IN THE EPOXY/ALUMINUM SYSTEM

Sample No.	Coupling Agent and Concentration	High/Low Shear Strength	Average (psi)
693-696	3% Weslink E	3360/3272	3313
697-700	5% Weslink E	3272/3024	3142
701-704	10% Weslink E	3564/3400	3510
721-728	15% Weslink E	2408/1404	1869
705-708	25% Weslink E	660/440	495
709-712	3% SWS-401	3448/3172	3316
713-716	5% SWS-401	3648/3292	3509
717-720	10% SWS-401	3732/3512	3630
761-764	15% SWS-401	3732/3448	3598
729-732	3% XZ-8-5066	3332/3092	3242
733-736	5% XZ-8-5066	3588/3200	3367
737-740	10% XZ-8-5066	3792/3488	3610
741-744	15% XZ-8-5066	2796/1248	2195

TABLE 14 (CONT'D.)

AGENT CONCENTRATION VARIATION IN THE EPOXY/ALUMINUM SYSTEM

Sample No.	Coupling Agent and Concentration	High/Low Shear Strength	Average (psi)
745-748	3% SS-4004	3292/2980	3149
749-752	5% SS-4004	3408/3228	3325
753-756	10% SS-4004	3428/3088	3324
757-760	15% SS-4004	3472/3296	3405

TABLE 15

COMPREHENSIVE TESTING IN THE EPOXY/ALUMINUM SYSTEM

Sample No.	Temp. (°F)	Additive and Concentration	High/Low Shear Strength	Average (psi)
905-912	200	Control	2748/2484	2621
889-896	200	5% SWS-401	2288/1762	1993
857-864	200	10% XZ-8-5066	626/484	567
841-848	200	10% Weslink E	1764/1334	1480
89-104	75	Control	3336/2976	3150
713-716	75	5% SWS-401	3648/3292	3509
737-740	75	10% XZ-8-5066	3792/3488	3610
701-704	75	10% Weslink E	3564/3400	3510
865-872	-320	Control	1916/1360	1562
873-880	-320	5% SWS-401	2236/1782	1908
881-888	-320	10% XZ-8-5066	2212/1592	1984
961-968	-320	10% Weslink E	1666/1222	1448

High temperature results indicate that all of the additives are harmful to adhesion, and cohesive failure prevails. The reason for this is not immediately obvious since (1) some improvement is realized at room temperature testing; and (2) the high temperature testing does not occur above the cure temperature used. One possibility is that the additive causes the glass transition (Tg) of the system to be decreased in the system to much less than 200°F. This would mean that with additives, the epoxy at 200°F is being tested when its amorphous phase is farther into the rubbery state than the control resin. In considering the chemical composition of the additives (a hydroxy functional silane and a phosphorus ester) this phenomenon is understandable. These materials may react with the resin to reduce its functionality thereby decreasing the crosslink density. If this reactivity and subsequent decrease in crosslink density are realized, a significant change in bulk properties will in turn be manifested in the thermal behavior of the resin.

To check this postulation, differential thermal analysis (DTA) was performed on samples of EPON-VIII with and without additives. The discussion and results of this phase of the investigation are given in Section 4.2.

4.1.2.2 Epoxy/Mild Steel System - Table 16 shows the results of the nineteen commercial agents used as additives at 1.0 wt-% concentration in epoxy on a mild steel substrate. It is seen that only four agents (SWS-442, SWS-441, 4-Ampip, and CHA) gave any substantial improvement in lap shear adhesive strength. Both SWS-441 and SWS-442 are alkylchloro silanes while the other two agents are either primary or cyclic secondary amines. Many agents seriously decreased adhesion when incorporated into the resin in this particular system.

TABLE 16

COUPLING AGENT SCREENING IN THE EPOXY/MILD STEEL SYSTEM

Sample No.	Coupling Agent 1% by wt	High/Low Shear Strength	Average (psi)
1-16	Control	2444/2092	2240
17-24	SWS-401	2312/2072	2155
25-32	SWS-403	2240/1900	2167
113-120	SWS-441	2376/2300	2321
97-104	SWS-442	2520/2100	2343
41-48	Z-6020	2000/1456	1794
33-40	Z-6040	2340/1580	2036
49-56	Z-6076	2144/1726	1968
57-64	XZ-8-5059	2204/1926	2105
129-136	XZ-8-5066	2316/2208	2278
161-168	A-151	1960/1444	1797
169-176	A-153	2048/1548	1780
177-185	A-174	2188/1520	1805

TABLE 16 (CONT'D

COUPLING AGENT SCREENING IN THE EPOXY/MILD STEEL SYSTEM

Sample No.	Coupling Agent 1% by wt	High/Low Shear Strength	Average (psi)
186-192	A-186	2128/1612	1857
193-200	A-189	2000/1680	1786
137-144	VOLAN	1830/1580	1709
145-152	SS-4004	1462/876	998
153-160	Weslink E	2508/2168	2296
293-300	4-Ampip	2400/2260	2341
453-438	CHA	2400/2308	2344

Shear strength values for mild steel bonded with EPON VIII adhesive with varying concentrations of CHA, SWS-441, 4-Ampip, and SWS-442 are given in Table 17. Concentrations of SWS-441 and SWS-442 above 1% (5, 10, and 15%) in EPON VIII inhibited polymerization to such an extent that the test bonds did not cure to hardness after ninety minutes at 93°C, the standard cure schedule. Even the 3% concentration of SWS-441 eventually proved unreliable because of its proximity to the inhibition level. For this reason, the 1% concentration of SWS-441 was chosen for comprehensive testing in this system as indicated in Table 18.

4-Ampip was tested at seven concentrations, 1, 3, 5, 10, 15, 20 and 25%. Because it had the unusual effects of increasing shear strength even at a 15% concentration and of effectively promoting a cure even at room temperature, the higher concentrations of 20 and 25% were tested, but were found to shorten pot life too much to allow bonding. It is interesting that impressive shear strengths were obtained using the substituted piperidine while permitting the resin to cure more easily at room temperature. It is also noteworthy that reproducibility in this system is excellent (± 0.5% at 15% of 4-Ampip).

This increased adhesion and short cure schedule may be caused by either the cyclic amino group or the primary amino function in the 4-Ampip. In an effort to establish which of these moieties is responsible, a similar compound was used as an additive, cyclohexylamine (CHA). This compound provides a primary amine as a reactive site but no cyclic secondary nitrogen. The results given in Table 17 show that CHA at 3% is equivalent to 4-Ampip at 15%. However, the CHA does not effect an improved cure as does the piperidine. This would infer that the bonding ability of 4-Ampip is due to the primary amine while the curing properties are due to the cyclic secondary amine.

TABLE 17

AGENT CONCENTRATION VARIATION IN THE EPOXY/MILD STEEL SYSTEM

Sample No.	Coupling Agent and Concentration	High/Low Shear Strength	Average (psi)
113-120	1% SWS-441	2376/2300	2321
289-292	3% SWS-441*	2630/2416	2526
97-104	1% SWS-442**	2520/2100	2343
293-300	1% 4-Ampip	2400/2260	2341
315-318	3% 4-Ampip	2372/2296	2332
319-322	5% 4-Ampip	2268/1808	2110
323-326	10% 4-Ampip	2370/2200	2293
327-330	15% 4-Ampip	2628/2600	2609
379-382	3% CHA	2628/2576	2598

* No data were obtainable for concentrations of SWS-441 greater than 3% in EPON VIII due to reactivity with resin.

** No data were obtainable for concentrations of SWS-442 greater than 1% in EPON VIII due to reactivity with resin.

TABLE 18

COMPREHENSIVE TESTING IN THE EPOXY/MILD STEEL SYSTEM

Sample No.	Temp. (^{o}F)	Additive and Concentration	High/Low Shear Strength	Average (psi)
379-386	200	Control	1662/1120	1382
387-394	200	1% SWS-441	1672/1400	1540
395-402	200	1% SWS-442	2488/2284	2378
455-462	200	15% 4-Ampip	383/267	331
439-446	200	3% CHA	2424/1624	1877
1-16	75	Control	2444/2092	2240
113-120	75	1% SWS-441	2376/2300	2321
97-104	75	1% SWS-442	2520/2100	2343
327-330	75	15% 4-Ampip	2628/2600	2609
379-382	75	3% CHA	2628/2576	2598
403-410	-320	Control	1200/946	1042
411-418	-320	1% SWS-441	1296/1058	1194
419-426	-320	1% SWS-442	1510/1302	1438

TABLE 18 (CONT'D.)

COMPREHENSIVE TESTING IN THE EPOXY/MILD STEEL SYSTEM

Sample No.	Temp. (°F)	Additive and Concentration	High/Low Shear Strength	Average (psi)
427-434	-320	15% 4-Ampip	993/707	845
447-454	-320	3% CHA	1666/966	1293

Table 18 shows the data for the comprehensive testing in the epoxy/mild steel system. It can be seen that SWS-442 proved to be the most beneficial coupling agent at both -320 and 200°F.

While 15% 4-Ampip demonstrated the greatest improvement of shear strength at room temperature, it essentially destroyed shear strength at both -320 and 200°F. SWS-442 demonstrated a remarkable ability to retain room temperature strength at the higher temperature and was the only additive at any concentration to demonstrate that ability.

4.1.2.3 Epoxy/Stainless Steel System - Table 19 gives the results of screening all additives in the epoxy/stainless steel system. It can be seen that SWS-403 and VOLAN increased adhesive strength by the greatest amount, and the two agents were chosen for comprehensive testing in this system. Most other agents were detrimental to adhesion. Data obtained from concentration variation of SWS-403 and VOLAN are given in Table 20. The degree of cohesive failure in the epoxy/stainless steel system appeared to be 100% for the control samples and for those additives producing values equal to or greater than baseline shear strength. The increase in concentration of VOLAN and SWS-403 did not affect the type of failure (cohesive failure was retained) but rather, apparently affected the physical properties of the resin in an adverse manner. This brought about cohesive failure at a lower shear strength which could not be compensated for by an increased surface adsorption by the additives. The two beneficial agents were subjected to extreme temperature testing, and the results are given in Table 21. It can be seen that the two additives involved increased shear strength only at room temperature. The decrease in shear strength at -320°F caused by the presence of coupling agent is not easily explained but is apparently a legitimate effect, for in the only

TABLE 19

COUPLING AGENT SCREENING IN THE EPOXY/STAINLESS STEEL SYSTEM

Sample No.	Coupling Agent 1% by wt	High/Low Shear Strength	Average (psi)
33S-48S	Control	3868/3272	3631
57S-60S	SWS-401	3564/3372	3466
61S-64S	SWS-403	3896/3524	3742
65S-68S	SWS-441	3280/3120	3206
69S-72S	SWS-442	3568/3188	3401
49S-52S	Z-6020	3276/3192	3248
53S-56S	Z-6040	3088/2368	2864
97S-100S	Z-6076	1784/1200	1487
93S-96S	XZ-8-5059	3716/3478	3684
85S-88S	XZ-8-5066	3696/3356	3487
101S-104S	A-151	3356/3104	3237
105S-108S	A-153	3020/2756	2939
109S-112S	A-174	3000/2704	2913

TABLE 19 (CONT'D.)

COUPLING AGENT SCREENING IN THE EPOXY/STAINLESS STEEL SYSTEM

Sample No.	Coupling Agent 1% by wt	High/Low Shear Strength	Average (psi)
77S-80S	A-186	3168/3116	3140
113S-116S	A-189	3032/2736	2905
81S-84S	VOLAN	4070/3930	4000
89S-92S	SS-4004	3560/3288	3466
73S-76S	Weslink E	2932/2876	2894
153S-156S	4-Ampip	2784/2640	2717
117S-120S	CHA	3096/2780	3003

TABLE 20

AGENT CONCENTRATION VARIATION IN THE EPOXY/STAINLESS STEEL SYSTEM

Sample No.	Coupling Agent and Concentration	High/Low Shear Strength	Average (psi)
121S-124S	3% VOLAN	3312/3008	3172
125S-128S	5% VOLAN	2976/2668	2818
129S-132S	3% SWS-403	3488/3140	3323
133S-136S	5% SWS-403	3172/2144	2723
137S-140S	10% SWS-403	2396/1656	2094
141S-144S	15% SWS-403	2592/1676	2184

TABLE 21

COMPREHENSIVE TESTING IN THE EPOXY/STAINLESS STEEL SYSTEM

Sample No.	Temp. (^oF)	Additive and Concentration	High/Low Shear Strength	Average (psi)
231S-238S	200	Control	3008/2208	2570
239S-246S	200	1% SWS-403	2000/1496	1718
247S-254S	200	1% VOLAN	2596/1748	2242
33S-48S	75	Control	3868/3272	3631
61S-64S	75	1% SWS-403	3896/3524	3742
81S-84S	75	1% VOLAN	4070/3930	4000
316S-319S	-320	Control	1640/1556	1610
320S-323S	-320	1% SWS-403	1518/1328	1452
324S-327S	-320	1% VOLAN	1668/1100	1399

other situation where SWS-403 was involved in comprehensive testing, the urethane/stainless steel system, it also decreased shear strength at -320°F (see Table 11). The type of failure involved in the cryogenic tests in the epoxy/stainless steel system was total adhesive failure (as it was in the urethane/stainless steel system) which indicates bonding hindrance at the substrate-resin interface created by the combination of cryogenic temperature and coupling agent presence.

The decrease in shear strength at 200°F caused by additive presence can be related to the explanations as given in Sections 4.1.2.1 and 4.2.

4.1.2.4 Epoxy/Glass Cloth System - In an attempt to determine the lap shear adhesive strength to glass, several approaches were investigated. In chronological order these were: using a 0.046" thick glass plate with epoxy adhesive between steel coupons, an identical system but with 0.005" thick glass, and finally several types of glass cloth.

As a result of deformation of the steel coupon in tension, the glass plates broke in every case, and the values listed in the top half of Table 22 are not true indications of glass-resin adhesion.

Next, several weaves of glass cloth (116, 181, and 1500), all with VOLAN finishes, were inserted between epoxy/aluminum lap shear specimens. The more coarsely woven cloths, 181 and 1500, gave no indication of adhesive failure to glass and demonstrated low shear strength, both factors in contrast to the closely woven 116 cloth. This finely woven cloth showed obvious adhesive failure and at a value just below that of a simple epoxy/aluminum system.

TABLE 22

GLASS ADHESION IN EPOXY WITH ALUMINUM AND STEEL CARRIER SUBSTRATES

Sample No.	Type Glass and System	High/Low Shear Strength	Average (psi)
1G-4G	0.046" glass plate with steel	900/532	746*
5G-8G	0.046" glass plate with steel	808/622	698*
9G-12G	0.005" glass plate with steel	1692/1466	1605*
13G-20G	VOLAN precoated #116 glass cloth with aluminum	3096/2820	3003**
21G-28G	VOLAN precoated #181 glass cloth with aluminum	2996/2544	2756***
29G-36G	VOLAN precoated #1500 glass cloth with aluminum	2728/1916	2476***
37G-40G 49G-56G	Cleaned #116 glass cloth with aluminum	3200/2852	2967**
41G-44G	Cleaned #181 glass cloth with aluminum	2688/2504	2619***
45G-48G	Cleaned #1500 glass cloth with aluminum	2982/2604	2716***

* Glass fracture obtained

** Adhesive failure to glass

*** Cohesive failure

Table 23 shows the results of coupling agent screening using #116 glass cloth in an epoxy/aluminum system. Of the nineteen agents screened, only Z-6020 showed substantial improvement of shear strength, and approximately half of the failure involved with this additive was a combination of cohesive failure and adhesive failure from the aluminum. This indicates that approximately 3300 psi is the maximum shear strength measurable in the epoxy/glass system using aluminum as the carrier substrate.

4.1.3 Bond Failure Analysis in the Lap Shear Systems - One of the more important aspects of this study involved recognition of the type of failure suffered by the test bonds under each condition. Shown in Table 24 is the average type of failure involved in each system at each of the three test temperatures. All of the urethane systems suffered essentially adhesive failure except the low temperature T-peel tests which were completely cohesive. This may indicate that additives in the urethane systems produced results which were more a measure of agent migration through the urethane resin to the bond interface than a measure of agent effect upon the bulk properties of the resin itself.

Conversely, the predominance of cohesive failure in the epoxy systems may be a measure of agent effect upon the bulk properties of the epoxy resin, an effect which was especially evident in tests conducted at 200°F with epoxy/aluminum and mild steel (see Section 4.2). It may also be that the additives maintained the interfacial forces above the cohesive ones. The increased adhesive failure experienced by the two types of steel at 200°F (totally adhesive in the case of stainless steel) suggests that the bulk strength of the resin approached, and for stainless, exceeded the respective bond interface shear strength values at that temperature.

TABLE 23

COUPLING AGENT SCREENING IN THE #116 GLASS CLOTH ADHESION IN THE EPOXY/ALUMINUM SYSTEM

Sample No.	Coupling Agent 1% by wt	High/Low Shear Strength	Average (psi)
30G-40G 49G-56G	Control	3200/2852	2967
161G-164G	SWS-401	2824/2712	2774
113G-116G	SWS-403	2848/2588	2696
165G-168G	SWS-441	2992/2824	2912
117G-120G	SWS-442	2852/2456	2603
145G-148G	Z-6020	3432/3160	3289
125G-128G	Z-6040	3164/2888	3028*
157G-160G	Z-6076	2760/2680	2704
177G-180G	XZ-8-5059	2904/2716	2801
181G-184G	XZ-8-5066	2924/2832	2893
169G-172G	A-151	2836/2716	2762
137G-140G	A-153	2744/2520	2594

* About 40% adhesive failure off the aluminum

TABLE 23 (CONT'D.)

COUPLING AGENT SCREENING IN THE #116 GLASS CLOTH ADHESION IN THE EPOXY/ALUMINUM SYSTEM

Sample No.	Coupling Agent 1% by wt	High/Low Shear Strength	Average (psi)
149G-152G	A-174	2760/2668	2703
153G-156G	A-186	2772/2564	2669
173G-176G	A-189	2776/2636	2728
109G-112G	VOLAN	2948/2760	2842
133G-136G	SS-4004	2588/2348	2497
129G-132G	Weslink E	3080/2984	3052
141G-144G	4-Ampip	2956/2708	2869
121G-124G	CHA	3180/3016	3120

TABLE 24

TYPE OF FAILURE EXPERIENCED BY TEST BOND (AS RELATED TO SYSTEM AND TEST TEMPERATURE)

System		Temperature		
Adhesive	Substrate	+200°F	+75°F	-320°F
Urethane	Aluminum	Adhesive	Adhesive	Adhesive
	Mild Steel	Adhesive	Adhesive	Adhesive
	Stainless Steel	Adhesive	Adhesive	Adhesive
	Glass	---	Adhesive (off glass)	---
	T-Peel	Adhesive	Adhesive	Cohesive
Epoxy	Aluminum	Cohesive	Cohesive	Adhesive
	Mild Steel	80% Cohesive 20% Adhesive	Cohesive	Adhesive
	Stainless Steel	Adhesive	Cohesive	Adhesive
	Glass	---	Adhesive (off glass)	---
	T-Peel	---	Cohesive	---

The total adhesive failure experienced at -320°F by all epoxy systems was apparently a result of thermal stresses imparted upon the organic/substrate interface; however, a legitimate agent effect upon the substrate-resin bond interface can be observed because of this.

4.2 Thermal Analyses of Adhesive Systems

Figures 3 and 4 are representative DTA thermograms of Adiprene L-100/MOCA (with and without additive) and EPON VIII epoxy (with and without additives) respectively. Figure 3 indicates that 3% Z-6040 affects the Tg of Adiprene L-100 very little, especially when the degree of migration of the Tg is compared to the difference between the test temperature and Tg_0 (control Tg). (The closer Tg is to the test temperature, the greater the effect of even a slight Tg migration, regardless of direction.) The glass transition temperature of urethane is apparently not greatly affected by the additives used (which indicates that additives' affects on adhesion in the urethane systems are detached from their Tg migration effects); therefore, the DTA program was centered around the EPON VIII epoxy adhesive and the effects of additives upon that adhesive's systems, which were significant.

It is plausible that the relationship between Tg and test temperature is responsible for the very great increases in adhesion of the urethane systems at low temperatures. That is, when it is cooled to -320°F, it passes from the rubbery state to far into the glassy region and therefore exhibits higher strength, even without additive, by a factor of 3 to 5 times, depending on substrate. On cooling the epoxy systems, however, which is already in the glassy state at room temperature, no strength gains are observed. In fact, epoxy adhesive experiences loss in strength at -320°F which may be attributed to severe thermal stresses introduced so far below the glass transition.

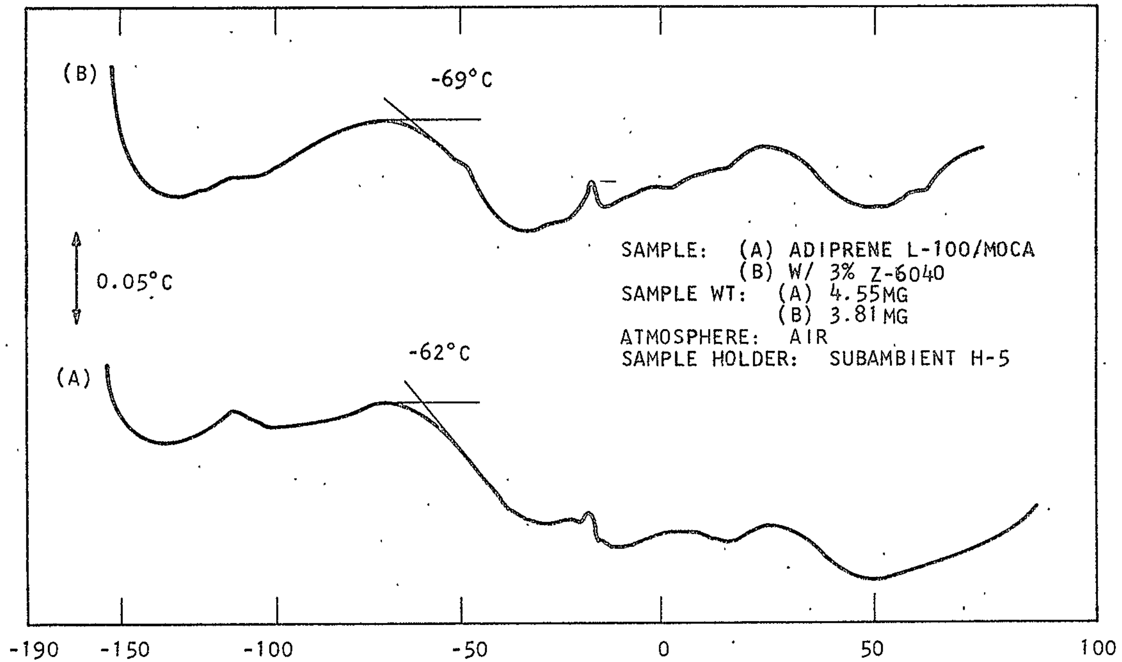


FIGURE 3

DTA OF URETHANE ADHESIVES

5/4/70 JOHNSON (WN)
46-191-35

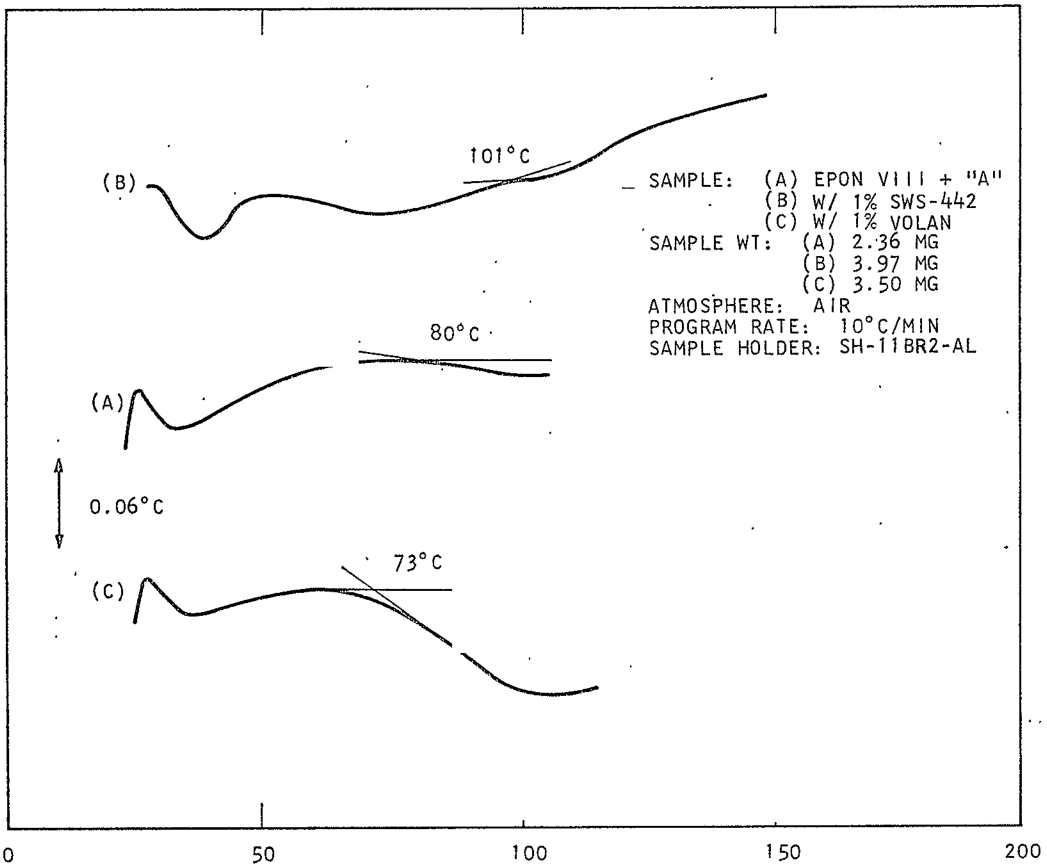


FIGURE 4

DTA OF EPOXY ADHESIVES

A6-191-34
5/4/70 JOHNSON (KN)

Because shear strength values at +200°F in the epoxy/aluminum system with additives dropped drastically from room temperature levels (see Table 15), it was postulated that the use of additives causes the Tg to be lowered from near the test temperature to far below it, thereby, causing a change in mechanical properties (modulus, hardness, elasticity, etc.) at 200°F. That is, with additives, the amorphous region of the epoxy at 200°F is well into the rubbery state while without agents, it is near the point where its mechanical properties approach those of the glassy state. These lowered bulk properties then bring about a decreased bulk strength (more cohesive failure) which cannot be compensated for by any increased surface adsorption of the additives At room temperature, of course, all compositions are far into the glassy state, and no detrimental agent effect is seen. On the contrary, some agents improve the situation since interfacial forces play a more important role.

Figure 4 presents an example of an additive which increased Tg (SWS-442) and one which decreased Tg (VOLAN) of the control epoxy. SWS-442 had the unusual and beneficial effect of increasing the glass transition temperature of the resin to a temperature above the test temperature. Only after DTA was it tested in lap shear at +200°F and found to also increase the strength of the system. It was not tested during the original program because its 75°F effects were minimal. This is an example of how DTA can be an effective screening tool. VOLAN lowered Tg of the resin and produced a consequential lowering of shear strength at +200°F.

Figures 5 and 6 exhibit shear strength at +200°F versus Tg data for both epoxy/aluminum and epoxy/steel in two ways. Figure 5 shows the obvious relation of shear strength to Tg in both systems. The epoxy/aluminum system demonstrated an almost

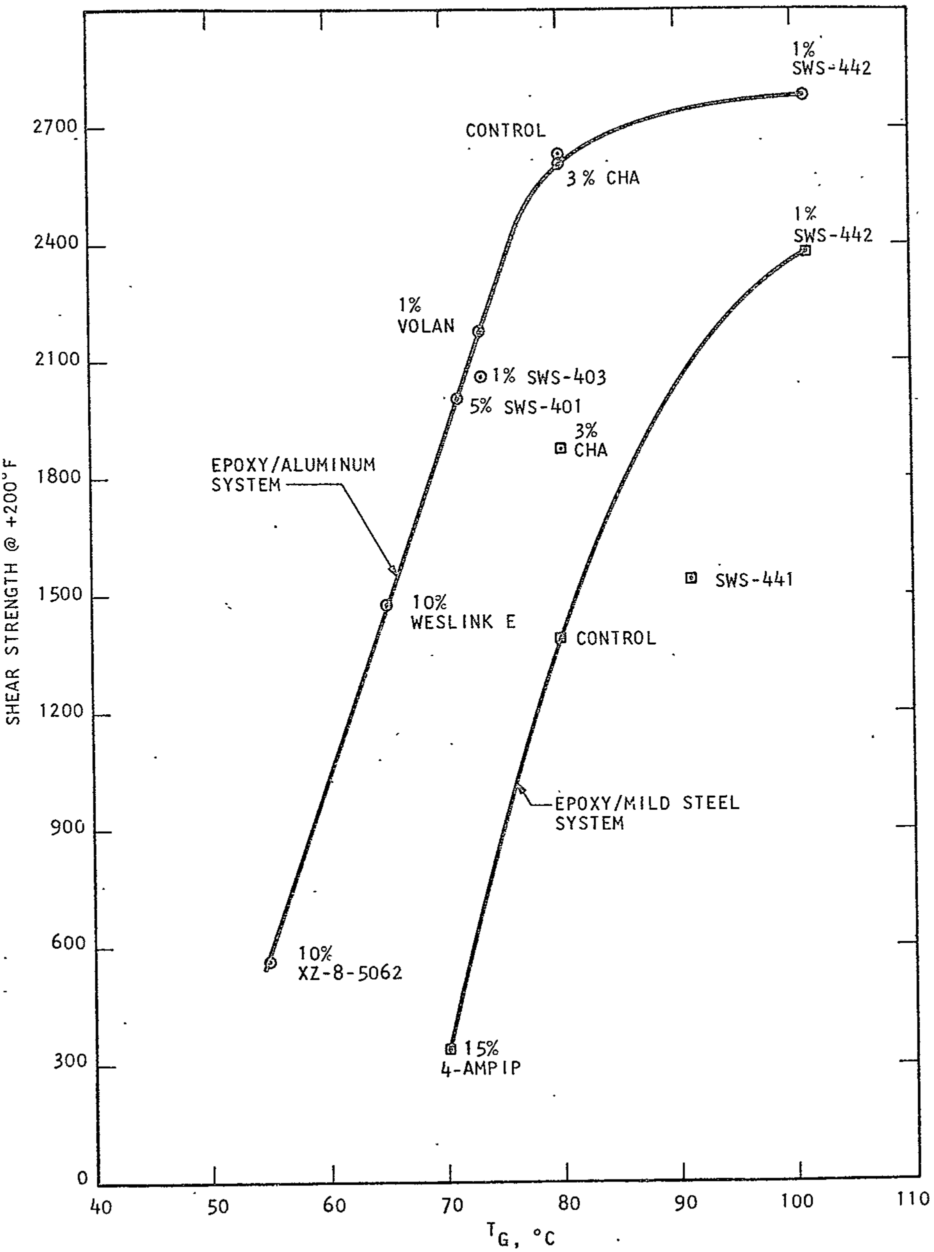


FIGURE 5

SHEAR STRENGTH-Tg RELATIONSHIP

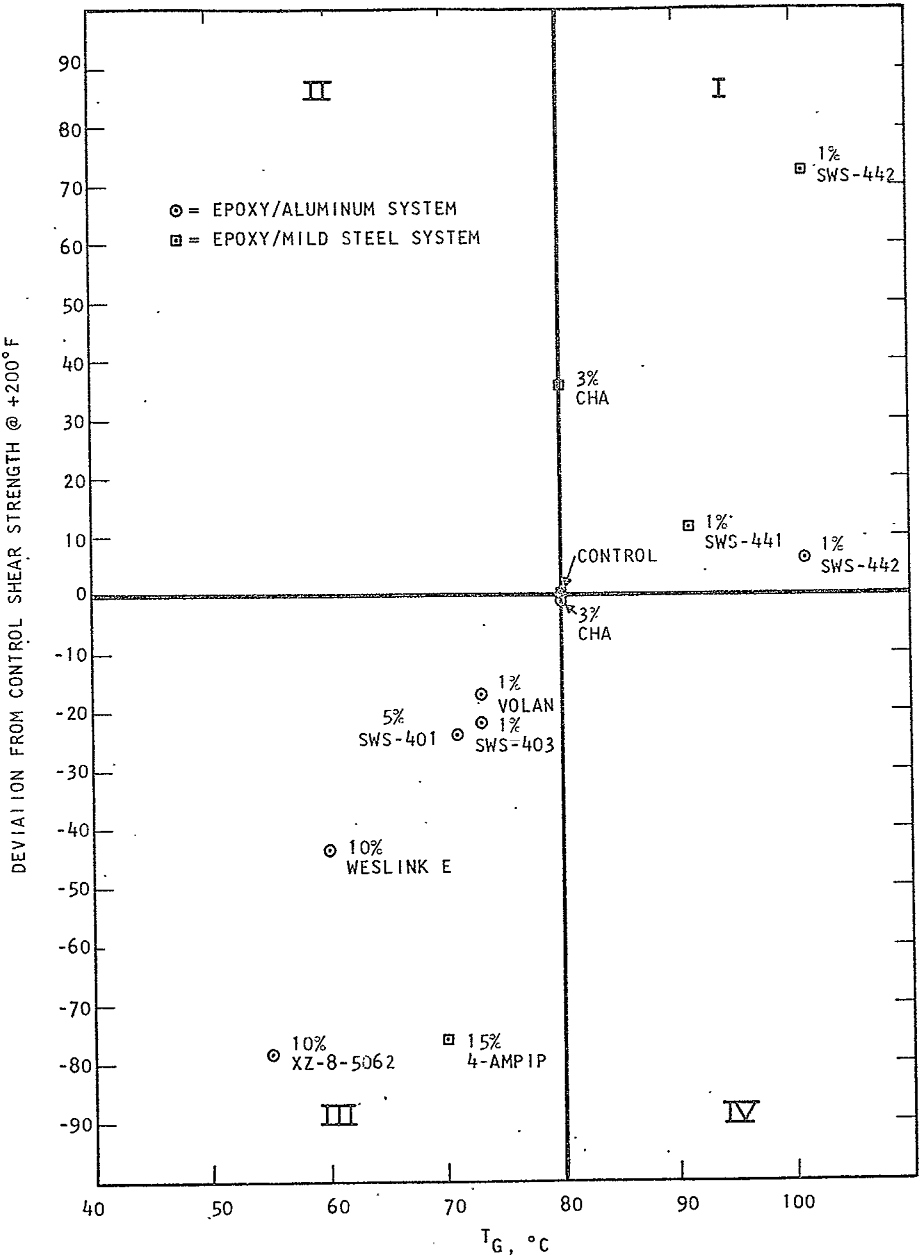


FIGURE 6
QUADRANT PLOT OF SHEAR STRENGTH vs Tg

A6-191-38 5/6/70 JJ (KN)

linear lap shear strength/Tg relationship while the epoxy/mild steel system did not demonstrate linearity so clearly. It must be noted before comparing the two systems, however, that the epoxy/aluminum system experienced essentially total cohesive failure at +200°F while the epoxy/mild steel experienced a combination of cohesive and adhesive failure. Since apparently only the cohesive failure of the epoxy resin is affected by Tg migration, the adhesive failure of the resin off the substrates in the epoxy/mild steel system at +200°F introduces a variability independent of Tg which destroys linearity of the shear strength/Tg relationship in this system.

The leveling off of the curves at high strengths may be a real effect and can be explained in two ways. First, as the glass transition of the system departs far from the control, the cohesive strength becomes less sensitive to changes in Tg. A second way to express this is to say that even at very high Tg, the cohesive strength approaches asymptotically a limiting maximum value which is the maximum bulk strength to be expected. Of course, it is probable that as this point is approached, more adhesive failure would be realized. There is, however, a third explanation; the Tg of the 442 mixture is above the test temperature and therefore the adhesive was in the glassy state. All other systems on this curve were in the rubbery phase; and, as a result, the two types of data points may not be directly comparable. That is to say, separate effects are being tested.

Figure 6 shows that both systems conform to the theory as postulated above. That is, if an additive increases Tg of the resin, it increases shear strength at +200°F. It is evident that the reverse is true also, for only the first and third quadrants of the graph are occupied by data points. If data points existed in the second and/or fourth quadrants, they could not be explained by the postulation as set forth above. It must be remembered however, that the type failure (cohesive vs adhesive) must be considered before the Tg/lap shear strength relationship of the resin can be determined. The greater the degree of cohesive failure of the resin involved, the more accurately shear strength can be estimated for a known Tg from a curve like those in Figure 5.

An intimate knowledge of the thermal history of the resin comprising the bond in question is also necessary before an accurate shear strength estimation is possible. The "elevated" cure schedule involved and any subsequent elevated thermal history of the resin directly affects its Tg which, in turn, affects shear strength. For instance, EPON VIII epoxy with 1.0 wt-% SWS-442 cured ninety minutes at 93°C has a Tg of approximately 100°C. If this epoxy (cured as above) is heated at 10°C/min until 121°C (250°F) is reached and then air quenched, the resulting Tg of the resin is approximately 87°C. An elevated cure schedule variation or thermal history will not necessarily always affect resin Tg adversely (lower it, as in the above case), for just as surely as there is an optimum cure schedule to establish maximum bulk properties in the resin at room temperature, there is one to establish maximum bulk properties in the resin at elevated temperatures (impart a maximum Tg of which the improved bulk properties of the resin at an elevated temperature would be a result). There is no guarantee that the two coincide.

4.3 T-Peel Tests

4.3.1 Urethane - Table 25 shows the results of screening those agents which were beneficial in the urethane/aluminum lap shear systems in the urethane/aluminum T-peel system. It can be seen that 1% Z-6040 increased T-peel strength by approximately 70% and 1% A-186 increased the strength by approximately 60%. One percent Z-6076 had no effect on T-peel strength while 1% SWS-401 and

TABLE 25

COUPLING AGENT SCREENING IN URETHANE/ALUMINUM T-PEEL TESTS

Sample No.	Coupling Agent 1% by wt	Average Peel Strength (piw)
10T-18T	Control	38.2
35T-43T	Z-6040	65.1
44T-52T	Z-6076	38.0
53T-60T	SWS-401	~4
61T-70T	Weslink E	~8
71T-79T	A-186	60.9
80T-88T	Weslink E	~6

Weslink E essentially destroyed T-peel strength. This latter effect was a reproducible one as can be seen in Table 25 by comparing sample numbers 61T-70T and 80T-88T.

Table 26 shows the results of comprehensive testing in the urethane/aluminum T-peel system. As they did at room temperature, 1% concentrations of Z-6040 and A-186 substantially increased T-peel strength at +200°F. At both +75°F and +200°F the test samples suffered total adhesive failure. However, at -320°F, the urethane was cooled through its glass transition temperature and far into its glassy state and suffered total cohesive failure. Consequently, the resulting T-peel strengths were very low and did not reflect the resin-substrate coupling ability of the agents involved. Furthermore, at -320°F, the urethane T-peel samples behaved much like the epoxy T-peel samples did at room temperature. This low temperature behavior for urethanes in T-peel is due to its being in the glassy state. (The epoxy was glassy at room temperature since its Tg was 93°C.) When a substance forming the bondline achieves a high modulus by becoming glassy, it is no longer able to relieve the high stress concentrations encountered at the leading edge of the bondline, and it fails catastrophically at relatively low tensile values.

4.3.2 Epoxy - Table 27 gives the results of the epoxy T-peel tests, but because of its brittleness, EPON VIII gave no significant data in a T-peel test. The adhesive simply broke along the bondline as a small peel force was applied. The bond suffered total cohesive failure and it can be seen that the presence of an additive had no appreciable effect on the peel strength.

4.4 Elastomers

Shown in Table 28 are the results of the screening efforts in the elastomer program. During the control value

TABLE 26

COMPREHENSIVE TESTING OF URETHANE/ALUMINUM IN T-PEEL

Sample No.	Temp. (°F)	Coupling Agent 1% by wt	Average Peel Strength (piw)
89T-95T	200	Control	19.8
96T-102T	200	Z-6040	41.7
103T-111T	200	A-186	27.4
10T-18T	75	Control	38.2
35T-43T	75	Z-6040	65.1
71T-79T	75	A-186	60.9
112T-120T	-320	Control	~9
121T-128T	-320	Z-6040	~6
129T-136T	-320	A-186	~7

TABLE 27

T-PEEL TESTS WITH 0.020" 2024-T3 ALUMINUM BONDED WITH EPON VIII EPOXY ADHESIVE

Sample No.	Coupling Agent	Average Peel Strength (piw)
19T-26T	Blank	2.7
27T-34T	1% Z-6040	2.3

TABLE 28

ELASTOMER - SCREENING

Sample No.	Filler and Agent	Average Tensile Strength (psi)	Average % Elongation to Break	Average Bulk Modulus (psi)	Average Young's Modulus (psi)	Average Yield Point Stress at 100% Elongation
48E-62E	Control	5576	553	1008	2506	1046
63E-76E	2% Cab-O-Sil No Agent	5131	504	1054	3194	1158
77E-89E	2% Cab-O-Sil 1% Z-6040	3622	520	704	2530	1130
90E-97E	No Filler 1% Z-6040	2888	485	596	2593	1060
98E-105E	2% Al_2O_3 No Agent	2808	493	571	2485	1163
106E-113E	2% Al_2O_3 1% Z-6040	3054	550	555	2400	1029
114E-119E	No Filler 1% VOLAN	2598	575	504	2895	946
128E-135E	No Filler 1% Weslink E	1952	516	400	2214	934

determination in the urethane/aluminum system, it was established that the thermal history of the Adiprene/MOCA mix has a direct relationship to its final properties, especially tensile strength. The fact that the elastomer urethane was heated prior to being mixed with the MOCA while the lap shear urethane was not should be remembered when comparing the physical properties of the two. However, it is a good approximation to assume that no degenerative effects were produced by the elevated thermal history of the elastomer urethane since the average control tensile strength of 5576 psi as established by samples number 48E through 62E in Table 28 is well above the minimum tensile strength of 4000 psi as established in the DuPont literature for Adiprene L-100/MOCA.

As seen in Table 28, no filler (Cab-O-Sil, Al_2O_3), agent (Z-6040, VOLAN, Weslink E), or combination of these increased the tensile strength of the elastomer.

Table 29 gives data obtained from the extreme temperature testing of elastomers as compared to that obtained at room temperature. The aforementioned lack of any effect also predominates at extreme temperatures.

TABLE 29

ELASTOMER - COMPREHENSIVE TESTING

Sample No.	Filler, Agent and Temperature	Average Tensile Strength (psi)	Average % Elongation to Break	Average Bulk Modulus (psi)	Average Young's Modulus (psi)	Average Yield Point Stress at 100% Elongation
136E-143E	Control +200°F	1,777	799	222	380	135
144E-151E	No Filler 1% Z-6040 +200°F	1,775	702	259	448	162
48E-62E	Control +75°F	5,440	550	965	2506	1046
90E-97E	No Filler 1% Z-6040 +75°F	2,888	485	596	2593	1060
153E-160E	Control -320°F	11,194	---	---	---	---
161E-168E	No Filler 1% Z-6040 -320°F	10,224	---	---	---	---

5. SUMMARY AND CONCLUSIONS

A two task investigation was conducted which resulted in considerable information on the benefits of incorporation of coupling agents in adhesives. Task I was a review of the past 20 years of the technical literature, compilation of all references on adhesives and adhesion promoters and finally preparation of a review article. This review with references is attached as an appendix and has been accepted for publication by Dr. Irving Skeist, Editor of "Reviews of Polymer Processing and Technology." This paper gives a background of adhesion theories and discusses in detail the three principal classes of coupling agents (silanes, phosphorus esters and chromic acid complexes) as well as a number of miscellaneous types. In addition, tables are given of commercial agents and their structures and comparison of effects of agents from published data. From this review it was obvious that there is still considerable debate on adhesion theories but that coupling agents would be operable in each. Also most work done with these agents has been on glass substrates and by preapplication of the agent prior to bonding.

The second task, an experimental evaluation, involved lap shear and T-peel adhesive tests, elastomer tests, and thermal analysis of the bulk adhesive. The materials of concern were epoxy and urethane adhesives and aluminum, mild steel, stainless steel and glass substrates. In general the process was to test each of 19 additives (chosen on the basis of structure to eliminate duplicate tests) in each system at room temperature. Table 30 gives the average for all systems screened at room temperature. From this the best additives were chosen and the optimum concentration was determined. Then the optimized systems were comprehensively tested at -320 and +200°F. A summary of all comprehensive tests is given in Table 31 which shows average lap

TABLE 30

COMPILATION OF AVERAGES FROM AGENT SCREENING (1.0 WT %) IN LAP SHEAR*

	Urethane				Epoxy			
Coupling Agent 1% by wt	Aluminum	Mild Steel	Stainless Steel	#116 Glass	Aluminum	Mild Steel	Stainless Steel	#116 Glass
SWS-401	1881	958	1210	1100	3303	2205	3466	2774
SWS-403	1537	1065	1262	1323	3229	2155	3742	2696
SWS-441	1300	732	994	1040	3212	2321	3206	2912
SWS-442	1017	603	222	1041	2983	2343	3401	2603
Z-6020	Incompatible				3156	1794	3248	3289
Z-6040	2166	1545	1220	1499	3212	2036	2864	3028
Z-6076	1905	1049	1150	1301	3126	1968	1487	2704
XZ-8-5059	1424	807	720	1111	3102	2105	3684	2801
XZ-8-5062 (5066)	1523	991	1040	731	3293	2278	3487 (5066)	2893

* The systems which were subjected to comprehensive testing are underlined.

TABLE 30 (CONT'D.)

COMPILATION OF AVERAGES FROM AGENT SCREENING (1.0 WT %) IN LAP SHEAR*

	Urethane				Epoxy			
Coupling Agent 1% by wt	Aluminum	Mild Steel	Stainless Steel	#116 Glass	Aluminum	Mild Steel	Stainless Steel	#116 Glass
A-151	1283	914	879	1265	3243	1797	3237	2762
A-153	1385	981	798	1017	3238	1780	2939	2594
A-174	1408	1010	1040	1237	3183	1805	2913	2703
A-186	1802	1096	1242	1286	3118	1857	3140	2669
A-189	1568	829	1446	1497	3209	1786	2905	2728
VOLAN	1571	983	1059	1189	3198	1709	4000	2842
SS-4004	1240	752	1012	1071	3291	998	3466	2497
Weslink E	1820	847	913	1211	3392	2296	2894	3052
4-Ampip	Incompatible				2995	2341	2717	2869

* The systems which were subjected to comprehensive testing are underlined.

TABLE 30 (CONT'D.)

COMPILATION OF AVERAGES FROM AGENT SCREENING (1.0 WT %) IN LAP SHEAR*

	Urethane				Epoxy			
Coupling Agent 1% by wt	Aluminum	Mild Steel	Stainless Steel	#116 Glass	Aluminum	Mild Steel	Stainless Steel	#116 Glass
CHA	977	921	688	865	3198	2344	3003	3120
Controls	1525	988	1130	1400	3150	2240	3631	2967

* The systems which were subjected to comprehensive testing are underlined.

TABLE 31

COMPILATION OF AVERAGES FROM COMPREHENSIVE TESTING (LAP SHEAR ONLY)

Adhesive	Substrate	Coupling Agent and Concentration	-320°F	Room Temp.	+200°F
Urethane	Aluminum	1% SWS-401	4761	1881	644
		1% Z-6040	8497	2166	997
		1% Z-6076	7997	1905	1062
		1% A-186	8414	1802	881
		1% Weslink E	6943	1820	1059
		Base	5023	1525	545
	Mild Steel	3% Z-6040	11088	1701	1074
		Base	4913	988	878
	Stainless Steel	SWS-403	4024	1262	650
		A-189	7187	1446	741
		Base	4388	1130	510

TABLE 31 (CONT'D.)

COMPILATION OF AVERAGES FROM COMPREHENSIVE TESTING (LAP SHEAR ONLY)

Adhesive	Substrate	Coupling Agent and Concentration	-320°F	Room Temp.	+200°F
Epoxy	Aluminum	5% SWS-401	1908	3509	1993
		10% XZ-8-5062	1984	2610	567
		10% Weslink E	1448	3510	1480
		Base	1562	3150	2621
	Mild Steel	1% SWS-441	1194	2321	1540
		1% SWS-442	1438	2343	2378
		15% 4-Ampip	845	2609	331
		3% CHA	1293	2598	1877
		Base	1042	2240	1382
	Stainless Steel	1% SWS-403	1452	3742	1718
		1% VOLAN	1397	4000	2242
		Base	1610	3631	2570

shear strengths for all systems run at -320 and +200°F. To conduct the testing at -320°F a special chamber was designed to fit on the lower jaw of the Instron. This chamber held the coupon in a bath of liquid nitrogen during test.

Five agents were beneficial at +75°F in the urethane/aluminum system (by 20-40%). Three of these are helpful (100%) at +200°F while four are effective at -320°F. The methoxysilanes appear to be useful moieties for surface interaction, and epoxy functions show that they are useful with urethane adhesives.

With a mild steel substrate only one agent is effective in urethane, and this was even more significant at low temperatures, although it did improve the strength at +200°F.

Only two agents showed significant improvements on stainless steel in urethane. Again the -320°F effect of the agent was greatest although an increase of 45% was realized at +200°F.

To test adhesion to glass a 116 glass cloth was imbedded in an aluminum bond line. It was shown that in this system the failure was adhesive from the glass so that a real test of the glass surface was possible. Essentially no benefits were derived from any of the agents in this particular application.

In general for the urethanes, the methoxy silane bond is beneficial in its ability to form surface bonds and improve bond strength while the chlorosilane function was detrimental. (It should be noted that the effects seen have not been proven to be due to primary bond formation at the substrate surface.) With respect to the organic portion of the agent, mercapto, epoxy and chloroalkyl groups are generally beneficial while vinyl and phenyl substituents are harmful to urethane adhesion. Of course, amino functions reacted too rapidly with the urethane to permit testing.

The epoxy/aluminum tests showed little effect (8%) with any agent. Also in the epoxy system the optimum concentration was found to vary considerably with additive type. At +200°F all additives used were harmful to adhesion while a maximum of 25% increase was obtained at -320°F. In an effort to determine the cause of high temperature failure, differential thermal analyses were taken on the bulk ahdesive to determine the glass transition temperature (Tg). A linear relation was found between adhesive strength at +200°F and Tg and it was postulated that the reactive additives decreased the bulk strength of the adhesive by lowering the crosslink density. This brings about increased cohesive failure at lower strengths. As a result it is proposed that Tg is a good indication of bond strength which may be possible at any temperature and also sets the maximum temperature at which an adhesive may be expected to be useful.

Four agents improved the epoxy/mild steel adhesion and one of these was effective even at +200°F. (This agent also increased the Tg and was the only one to do so.) At this time 4-aminomethyl piperidine (4-Ampip) was found to be a good curing agent at room temperature because of its cyclic secondary amine and a good adhesion promoter because of its primary amine function.

In the stainless steel/epoxy system two materials were beneficial but only at room temperature.

For those agents that were generally effective in the epoxy system little is known of their structures. There are some silanes, a phosphorus ester and a chromic acid complex. As may be expected the agents which were most beneficial here were different from those found with urethane.

T-peel tests were conducted only with the aluminum/urethane. The epoxy adhesive was too brittle to give good experimental data. Only two agents increased strength here although five were active in the lap shear tests. These two materials were also good at +200°F but detrimental to peel strength at -320°F. This was due to the fact that at -320°F the adhesive is in its glassy region where it is more brittle and less able to relieve the severe bond line stresses encountered in this test.

When testing elastomers it was found that no filler, agent or combination of these would increase the tensile strength. Other physical properties were not significantly changed.

6. ACKNOWLEDGEMENTS

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A REVIEW OF COUPLING AGENTS AS ADHESION PROMOTERS

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ABSTRACT

An extensive review has been made of the literature from 1950 to the present to include all work in the area of coupling agents and their use toward improving adhesion. The types of agents studied, mechanisms by which they act, substrates, adhesive systems and theories of adhesion are all considered.

By far the most common system is silane agent on a glass substrate, and a covalent siloxane linkage is proposed as the operative mechanism. Phosphorus esters and chromium-acid complexes are also known to be effective, and similar mechanisms are postulated. Other species will adsorb on adherend surfaces to provide an adhesive interlayer.

The use of coupling agents as admixtures with adhesives and the use and mechanisms of their behavior on metallic substrates has not been thoroughly studied until recently.

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I. INTRODUCTION

The science of adhesion, although studied for years, is now experiencing serious investigation of the interfacial molecular forces responsible for this phenomenon. Discussions have arisen over the relative effects of chemical bonding and physical wetting, the best methods to obtain the optimum in each instance, and the role of adsorbed species and weak interfacial layers. It is not the purpose of this review to discuss the entire science of adhesion, but to concentrate on one area of increasing importance: the formation of a primary chemical bond linkage between a non-organic substrate and an organic adhesive system by the use of a coupling agent.

The fact that coupling agents are considered a principal factor in adhesion states a priori that the primary chemical bond is of considerable importance in adhesives. This is not as readily accepted as it may appear and is certainly not the whole story. Other matters which must be considered are wetting, interlayers, bulk properties, adsorbed species, environmental effects, etc. One should recognize that all of these parameters play important roles which cannot often be clearly separated.

Wetting of an adherend by the adhesive is, of course, necessary for good adhesion as shown many times over. After all, the function of the adhesive is to provide and maintain intimate contact between two solid surfaces. This is accomplished by having a liquid adhesive with a surface tension (γ_{LV}) which is less than the critical surface tension of wetting (γ_C) of the solid surface.[346] When this condition exists, the liquid forms a low (zero) contact angle with the substrate which denotes wetting and spreading on the surface. However, it is when one considers the micromechanics of the adhesive process that questions arise as to the contribution from chemical bonding. It appears that primary chemical bonding to the substrate or the resin does indeed make a contribution although it is difficult to quantify.

Coupling agents may be used to form primary bonds to either or both the adherend and the bulk adhesive. The bond to the organic adhesive can occur by virtue of a reactive function on the agent similar to the monomer used or one which is reactive with the monomeric species. That is to say an agent may contain a terminal epoxy or vinyl moiety which will copolymerize with the organic system it contacts; or the agent may contain a function such as an amine which will cure an epoxy or urethane resin at least in part. Examples of each of these will be discussed below under the specific systems presented. However, wit a polyester-glass system, the non-reactive silane, an amino alkyl silane, was shown to be detrimental to the physical properties. Evidently, it is possible for a release agent effect to occur if primary bonding does not exist between the agent and the organic phase.[78a]

Adhesion promoters which do not bond primarily to the resin phase are commonly long-chain fatty acids terminally substituted with p-chlorophenyl groups.[225, 274, B-3] It is postulated for these compounds that the carboxylic acid end groups are used to adsorb to surfaces of glass, metal and ceramic, while the pendant alkylphenyl groups offer a hydrophobic, resin-soluble phase.[10, 53, 275, 144, 180] These particular agents also increase the critical surface tension of the substrate to promote wetting.[263] However, in some instances, although the agent has the proper reactive moieties, it will decrease γ_C so that the adherend is wet only with difficulty.

There are, of course, two bonding mechanisms by which an agent can attach itself to a surface: simple Van der Waals attraction (dipole-dipole) or actual bond formation of a chemical bond by exchange of electrons. The first is evidenced by studies elucidating the relative adherence of substances with varying polarity of functional groups.[303] Studies with polymers containing acid and amide functional groups showed that both functions improved peel strength but that the former was superior.[188] It was concluded that electron availability contributes more than does dipole moment to interfacial interactions and therefore adhesion. This view corresponds to that which states that certain functions, such as piperidine, are chemisorbed to certain metallic surfaces, such as iron, to produce a relatively strong bond effective in adhesives, coatings or corrosion inhibitors.[12] This chemisorption phenomenon has been postulated to take place by virtue of the donation of the unbonded pair of electrons on the nitrogen to the unfilled 'd' orbital of the surface iron atom.[12, 97b, 115b]

Adsorption of simple polar long-chain compounds has been broken into three types: physical, chemisorption, and precipitated adsorption. The last two of which are very selective on metallic substrates. The mechanical properties and solubilities of each of these adsorbed films are distinctive.[330]

The formation of a direct primary bond, postulated for many coupling agents in the silane,[290] chromium complex,[121] and phosphate ester[267] classes, formerly was studied almost exclusively on glass substrates. Recently, however, such studies have been extended to metal surfaces.[54b, 304] The commercially available materials are compounds (M-X) which can be hydrolyzed to give reactive MOH functions which subsequently react with the SiOH surface functions by dehydration to form a very stable Si-O-M bond. These materials are generally used as a surface pretreatment prior to bonding and are partially polymerized on the substrate before addition of adhesive. An entirely new surface then presents itself to the adhesive, a surface which is wettable and reactive with the polymer.

Epoxy resins form their own primary bonds to some extent. Free radicals which form during the cure produce chemical bonds with metallic adherends.[21, 22] In the realm of attaching adsorbable functions to the polymer backbone some limited success has been seen.[102b, 253] Where one has the bondable functions on the backbone of an applied polymer new considerations are necessary. One is that in order for the groups to be effective and reach the substrate surface, the conformational energy of the polymer chain must be overcome. That is, the adsorbable functions must become aligned and in doing so possibly distort the normal chain equilibrium conformation.

However, when a polymeric rather than monomeric adsorber is utilized, significant increases in the adhesion of monomolecular layers is realized. This was dramatically shown for corrosion inhibitors of various molecular weights where a degree of polymerization greater than 4 (adsorbable units) gives an increase in corrosion inhibition by a factor of 10,000.[12, 97b, 115b] The cause of this synergistic effect has been discussed in terms of the equilibrium between each chemisorbed group and the surface. With a multitude of bonded moieties on a polymer backbone, those few which are temporarily non-bonded in equilibrium cause essentially no disruption in overall attachment of the polymer.[343]

Recent work has elucidated the role of the resin in the vicinity of the interface, where, through coupling agents, a modified region of adhesive is produced.[157] With no agent and poor adhesion, debonding and failure occur at the interface.

However, with covalently bonded agents, failure is essentially cohesive deep in the resin body rather than adhesive at the substrate. (Good adhesive systems usually fail cohesively.) Further improvement is realized when an additional "inner layer" or "interphase" is introduced.[157, 198] This intermediate layer has been used on a macro-scale by mixing the adhesive and agent in high concentration and applying in a thin coat as a prebonded primer.[202] It is postulated through mathematical stress and modulus analyses that a thicker interphase will enhance yield stress. This region of modified resin is an extension of that produced by a monomolecular layer of the coupling agent. This serves to decrease the stress concentrations over a larger distance and to increase bond strength between two drastically different materials.

It is also possible, however, to effect an apparent increase in bond strength without changing interfacial forces. If one plasticizes the bulk adhesive an increase in strength is seen. This is due only to absorption of energy by the organic matrix.

The use in composites is an indication of what is seen in filled polymeric systems. As would be expected, as one increases the interaction between filler and organic matrix, the effect of the filler is magnified.[217] Stated another way, the ability of the fillers to enhance matrix properties is limited to and dependent upon the state of bonding at the polymer--filler interface.[25] Fillers show an effect similar to that of increasing the crosslinks in a system, e.g., an increase of glass transition temperature. This is due to the fact that polymer-surface interactions tend to limit the mobility of the polymer molecule much as does crosslinking.[180, 181, 302] Coupling agents then decrease the molecular mobility at the surface even more effectively than simple surfaces and essentially do produce a crosslink at the surface. This was shown by impregnating glass fibers with $TiCl_4$ and placing these in an olefinic monomer, styrene, resulting in initiation of polymerization at the glass surface. The formation of a chain coagulation structure of particles when properly treated[306] is possible. Thus, a polyvinylchloride filled with TiO_2 which was modified with octadecylamine demonstrated this ultimate effect of fillers.

Aside from initial bond strength improvement there have been two other distinct advantages generally recognized as being due to coupling agents. These are: (1) a lesser dependence on cure schedule for optimum strength, and (2) a resistance to bond strength degradation by aging or moisture. The second and perhaps more serious effect has been borne out experimentally on glass reinforced thermoset and thermoplastic systems[76, 229, 338] and with metal-polyurethane bonds.[304] This phenomenon is attributed by DeLollis to the fact that water is preferentially adsorbed on the substrate with subsequent displacement of any adhesive which is not primarily bonded. However, when a coupling agent is utilized, a primary bond is formed to the adherend surface which is not susceptible to hydrolysis or displacement by water. Thompson and Hill[304] have also noted that when a silane adhesion promoter is used in a urethane adhesive the original strength of a water saturated weakened bond can be regained by drying the sample.

The first effect, dependence of bond strength on cure schedule, was elucidated when lap-shear strength was determined for an epoxy-aluminum system with varying cure schedule.[54c] This strong dependence of adhesion on cure schedule was decreased considerably by the use of coupling agents. This means that manufacturing procedures can be less strictly controlled.

Certain generalities are worthy of note from this review. (1) Most of the work on coupling agents, both from a practical and theoretical standpoint, has been done on glass substrates. Recently, however, there has been increasing interest in the effect of coupling agents on metal surfaces.[54b, 304] (2) Most experiments have been done by pretreating the surface with the coupling agent prior to application of the adhesive. Again, interest is developing in the incorporation of the agent into the adhesive system because of the economic advantage of a single application.[54b, 304] However, the integral mixture requires not only that the agent migrate to and react at the substrate surface, but also that functional groups be similar in reactivity to the resin so that polymerization is realized only when desired.

The following sections discuss in detail all coupling agents known through June, 1969. The three principal types are silanes, chromium complexes and phosphorus esters which are discussed separately. A final section is a review of many miscellaneous surface agents on which some experiments have been run. A table of comparative data is also given.

The bibliography has been selected from over 1100 references on this subject since 1950. Its alphabetical listing by authors is supplemented by location of the abstract in Chemical Abstracts. Furthermore, following each reference is a series of numbers indicating subject matter dealt with therein according to the following code. A second portion of the bibliography, Part B, is a compilation of books and review articles on coupling agents and adhesive technology.

I. Adhesive
  1. Epoxy
  2. Urethane
  3. Elastomer
  4. Polyester
  5. Phenolic
  6. Silicone
  7. Other

II. Substrate
  11. Copper
  12. Aluminum
  13. Steel
  14. Glass
  15. Rubber
  16. Plastic
  17. Other

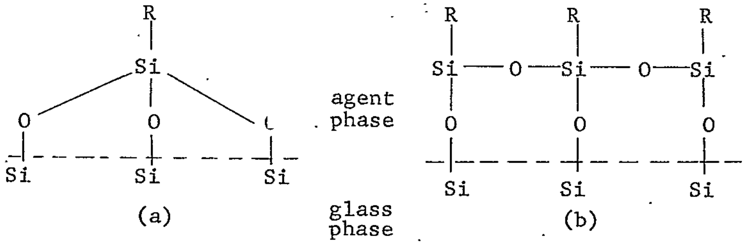
III. Agent Type
  21. Phosphorus
  22. Chromium
  23. Piperidine
  24. Silane
  25. Other

IV. Miscellaneous
  31. Environmental Effects
  32. Surface Chemistry
  33. Surface Preparation
  34. Fillers
  35. Test Methods

II. SILANES

A large number of silanes of general structure $R_{(4-y)}Si\,X_y$ have been evaluated as coupling agents. In these compounds the R groups are organofunctional groups which can be chosen for a specific purpose. The X groups may be halides, alkoxides, and/or acyloxy groups -- all of which are hydrolyzed under the conditions of application to give $Si(OH)_y$ groups. These silanol groups may in turn react with polar surface groups of the substrate by dehydration to form a primary bond. Thus, the molecule is ambifunctional; it contains polar silanol groups capable of adhering to the surface of glass, metals, etc., and a group R tailored to interact with the adhesive resin.

The adherence of the polar hydroxyl groups to the surface of glass is postulated to be through an ether type (siloxane) linkage between the SiOH groups of the glass and the $Si(OH)_y$ groups of the silane. Each molecule has the possibility of forming y Si-O-Si bonds. Whether the siloxane bonds are all formed



(a) (b)

with the glass surface (as in a) or with adjoining silane coupling agents (as in b) is still in question. However, it is known that the greater the possible number of siloxane bonds, the greater the stability of the linkage between coupling agents and the surface.[343] Further, kinetic studies have shown an increase in bond order between silane and glass in the order of mono-, di- and trichlorosilane.[117] Consequently, hydrolysis is more difficult and water stability is greatly enhanced for glass-resin bonds using as coupling agents silanes of the type R-SiX_3. While many silanes have been tested[19, 156, 336, 326] it is logical that the most effective and commercially available coupling agents have the general structure, $RSiX_3$.

Considerable work has been done in an attempt to determine whether the interaction between substrate and silane is actually a chemical bond as postulated above or simply a physical adsorption. Thermograms of the treatment of quartz powder with CH_3SiCl_3 vapor show a pronounced exothermic effect which is explained in terms of bond formation. Silanes with fewer X groups, $(CH_3)_2SiCl_2$ and $(CH_3)_3SiCl$, show proportionately weaker bonds.[11] These results were further substantiated by infrared spectroscopic studies of deuterated glass surfaces which showed weaker bonding on mono- and difunctional silanes as compared to the trifunctional silanes. Only external hydroxyl groups of the glass were found to react and these on a 1:1 basis with $(CH_3)_2SiCl_2$ and $(CH_3)_3SiCl$. The CH_3SiCl_3 reacted more on a 1:2 and 1:3 basis with the glass hydroxyl groups.[52, 59, 102, 117] Isotopically labeled (^{14}C) silanes have also been used to examine the extent of reaction with glass surfaces. Tracer and photomicrographic studies indicate continuous films instead of islands of the coupling agent with covalent bonds at the surface. Failure of the film in boiling water was attributed to failure of the glass substrate and not the glass-silane interface.[145, 325]

A novel investigation of the electronic interaction between coupling agent and glass substrate involved the determination of charge developed by stripping films of polymers from the glass surface. With untreated glass, the charge on the stripped film was negative, but it was positive when the glass had been treated with silane.[167, 168] The study is indicative of greater electronic used and the type of interaction possible. Obviously, compatibility of the R groups and the resin is necessary even in the case of the non-reactive silanes. To provide compatibility, polarity of the resin should match the polarity of the functional group to the extent of matching the degree of hydrogen bonding in each. A summary of the various reactions which may occur between resins and functional groups has been prepared by Plueddemann, et.al.:[242]

(1) Condensation reactions are possible between hydroxyl, carboxyl, mercapto, amino, or epoxy groups on silicon with hydroxyl or carboxyl groups of a polyester.

(2) Olefinic hydrocarbons or unsaturated ether and ester groups on silicon may participate in free-radical-induced addition polymerization with an unsaturated polyester and styrene monomer.

(3) Almost all functional groups are capable of reacting with an epoxy resin or its curing agent in an epoxy laminate.

The third class, the catalytic silanes, contain amino groups which can act as catalysts in the polymerization of phenolic, urea, and melamine resins and can act as curing agents for epoxy[17,160, 183, 294, 296, 313] and polyurethane[6] resins. Thus, the coupling agent is integrally involved with and bonded to the bulk adhesive. Examples of the amino groups present in commercially available catalytic silanes are $-(CH_2)_3-NH_2$, $-(CH_2)_3-NH-(CH_2)_3-NH_2$, and $-(CH_2)_3-NH-(CH_2)_2-NH-(CH_2)_2-CO_2CH_3$.[9, 15, 85, 102a, 118] In reaction with some adhesive systems, the amino silanes may be classified as simply reactive silanes and not catalytic. As such the amino group is capable of reacting with alkylhalides, acids, anhydrides, and esters in substitution or condensation reactions (Oddly, the amino silanes give poor adhesion to polyester resins, perhaps because of amine inhibition of the polyester cure.)[242]

interaction than can be explained by simple absorption of the coupling agent. Chemical methods have also been used with some success to study glass-silane interaction.[19, 171, 337]

Although silanes are useful as coupling agents on substrates other than glass (aluminum, steel, copper, etc.)[54b, 304] no definitive work has been published on the mechanism of interaction between the silane and these surfaces. Proposed mechanisms involve either a silanol-type interaction with surface oxide or hydration layers, or chelation of the metal by aminoalkyl groups of the silane.

Silane coupling agents can be divided into three classes according to their reactivity with the organic phase, non-reactive reactive, and catalytic, and are discussed below accordingly.

Non-reactive silanes have R̲ groups which are alkyl or aryl with no unsaturated or other reactive moieties. With a short alkyl group as in CH_3SiCl_3, a finish which is non-adherent to polar substances such as water and polyurethanes can be imparted to surfaces.[19, 80, 94, 102a, 103, 104, 163] However, methyl silanes have been used with excellent results as a primer for silicone rubber bonding to many surfaces.[120] Usually longer alkyl groups,[84, 278] aryl groups,[78a, 32, 226, 332] aralkyl groups,[221, 225] and halogenated derivatives of these groups [122, 225, 259] are incorporated in the silane for cohesive interaction with the bulk adhesive.[116, 197, 239, 278] Such groups are effectively used with non-polar resins such as polystyrene and other poly-vinyl compounds

Reactive silanes contain a function capable of chemically reacting with the bulk adhesive commonly as a comonomer. Reactive functions commonly employed are vinyl groups,[9, 61, 111, 114] epoxides,[31, 33, 34] mercaptans,[105] alcohols,[106, 175] phenols,[197] acids,[60] esters,[82, 85] and combinations of these functions.[153, 281, 295] The choice of reactive group depends on the adhesive to be

Silane coupling agents are usually applied to a glass substrate surface as a pretreatment from a dilute aqueous solution. Acid or base is added to the solution to aid in the hydrolysis of the SiX groups to SiOH. The solution is necessarily dilute (0.5-1.0% coupling agent) since optimum coupling effect is achieved with a mono-molecular layer rather than a multi-layer film of the silane. The surface is then dried, usually at temperatures over 100°C, to promote the condensation reactions and to remove excess water. Vapor phase application of alkyl-alkoxy silanes is accomplished by mixing the silane with moist air for hydrolysis and applying it to nascent glass surfaces while the temperature is held near the decomposition point of the silane.[89]

Some integral blending of the coupling agent into the adhesive resin has been tested with encouraging results.[6, 27, 36, 54b, 87, 97a, 105, 108, 115a, 123, 158, 234, 290, 292, 304] For example, outstanding improvement of metal bonding has been reported when silane coupling agents were integrally mixed with urethane and epoxy adhesives.[54b, 304] Such application has the economic advantage of reducing the number of steps required in the adhesive process. However, this advantage is somewhat negated in the usual procedure for integrally mixed adhesive systems because (1) a slower curing process may be needed to allow migration of the coupling agent to the substrate surface and (2) an excess of coupling agent is usually required since apparently all of the coupling agent does not reach the adherent surface.

The preceding discussion has dealt primarily with silane glass surface systems. More work has been published in this area than about other substrates because of the long-time interest in glass lamination in composites. However, silane coupling agents, as surface pretreatments or as mixtures, are being used increasingly in the bonding of metal substrates with a variety of adhesives.[54b, 304] The brief discussion below of some of the systems which have been reported will give some indication of the extent of such usage.

First, it should be noted that improved properties other than total strength may be obtained through the use of silane coupling agents with certain adhesive systems. The results of a long-term aging study have shown that more reliable and much improved adhesive properties were achieved when silane coupling agents were used with polyether-based polyurethane adhesive on aluminum. During a three-year period, loss of strength with normal variations in atmospheric humidity has been minimized, and greatly increased strengths at room temperature and +200°F have been observed.[304b] Furthermore, the samples utilizing a coupling agent can be dried to reproduce the original strengths.

Copper, treated with aminoalkyl silane compounds, was effectively bonded to silicone elastomers with exceptional bond stability at elevated temperatures.[34, 234a] Considering the substrate and adhesive, the probable mechanism was the chelation of the copper with the amino groups.

Aluminum has been treated with silanes to improve bonding with several adhesives. Bonding to silicone elastomers was enhanced either by amino silanes incorporated into the silicone[49, 70, 182, 248, 249] or by methyl silane treatment of the metal surface.[97, 120] Vinyl silane treatment of the metal also aided the adhesion of silicone elastomers.[138, 156] Adhesion of polyvinylhalides to aluminum and steel surfaces was increased by addition of amino silanes.[277] Polyurethane bonding of aluminum was greatly increased (particularly at +200°F) by surface treatment of the metal with an amino or epoxy containing silane.[304] Furthermore, incorporation of amino and epoxy silanes into the polyurethane adhesive has been tested on aluminum with good results.[54b, 87, 260, 304a,b] Amino and mercapto silanes have been proved effective as integral parts of adhesive mixtures of epoxy,[54b] phenolic, and polyvinyl butyral resins.[244]

Steel plates bonded with an epoxy-silane-modified polyurethane adhesive withstood 24 hours in boiling water as compared to only one hour with the unmodified adhesive.[6] Similarly, the incorporation of an epoxy or amino silane into an epoxy resin increased the sea-water resistance of the resin coating on steel.[30, 86] This serves to point out the contention that the primary benefit of coupling agents may be their effect on aging characteristics rather than on total initial strength of the adhesive.[76, 304] The proper choice of coupling agents will also allow effective bonding of "contaminated" steel. An epoxy silane treatment of oily or rusty steel increases the lap-shear strength of epoxy bonds over those of clean metal or untreated contaminated metals.[85]

Bonding of rubber to metal substrates such as copper, aluminum, or steel was improved by the use of amino silanes either as a pretreatment of the surface or by incorporation into the rubber.[182, 248] Similarly, amino-silane treated glass showed better adhesion to synthetic rubber such as neoprene.[191] In addition, a "double" treatment of glass with (1) an unsaturated silane followed by (2) an elastomer containing a free-radical curing agent was shown to increase the adhesion to natural or synthetic rubber.[317]

Use of coupling agents in bonding of plastic materials usually has been limited to lamination procedures in which the silane was applied to the reinforcing material and the organo-functional group interacted with the resin as it polymerized.[191, 210, 258, 282, 316, 319, 323] A study of the structural features of silanes which increase wet and dry flex strength of glass-polybenzimidiazole laminate at high temperature (600°F) has concluded that two conditions are necessary: (1) a stable aromatic bond to silicon and (2) a reactive functional group for bonding to the resin. Thus, cyanophenyl, carboxyphenyl, and bromotolyl groups were adjudged as most effective.[238]

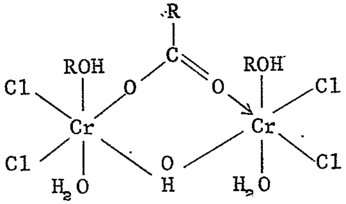
Surface treatment -- polymeric adherends with coupling agents has been done.[124] Impregnation of polyester and polyamide fabrics with glycidyl silanes has been used as a pretreatment for coating the fabrics with silicone rubber prior to polymerization and vulcanization.[81] Amino silanes have been used to treat a polyester film used for heat-pressure bonding to polyethylene film to give a highly water-resistant bond.[83]

Some substrates to which silanes have been applied must be termed "miscellaneous." A priming of clay surfaces by amino silanes is claimed to increase the adhesion of polyurethane and epoxy coatings and to aid in the water resistance of these coatings.[287] Several adhesive mixtures have been formulated which contain various silanes as integral constituents. These adhesives have been effectively applied to a variety of substrates: paper, brass, wood, ceramics, etc.[57, 271]

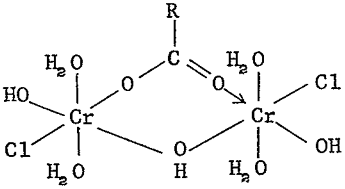
Much of the preceding discussion has centered on the use of silanes with the widely used adhesives--the epoxides, urethanes, polyesters, etc. The development of new adhesive resins such as polyimides, ionomers, and polysulfones will require the development and evaluation of more silane coupling agents tailored for each of these resins.

III. CHROMIUM COMPLEXES

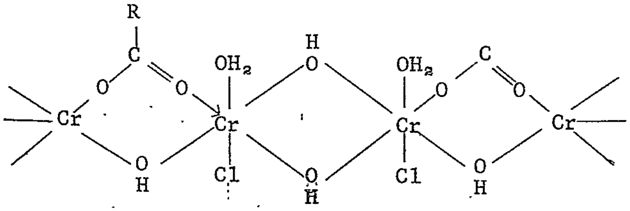
Trivalent chromium complexes which include an organic acid anion as one of the complexing species are widely used as coupling agents. The charge on the complex is determined by the coordinating groups which may be anions (usually chloride ions) or neutral molecules (water or alcohols). The structure of such a complex may be pictured as:



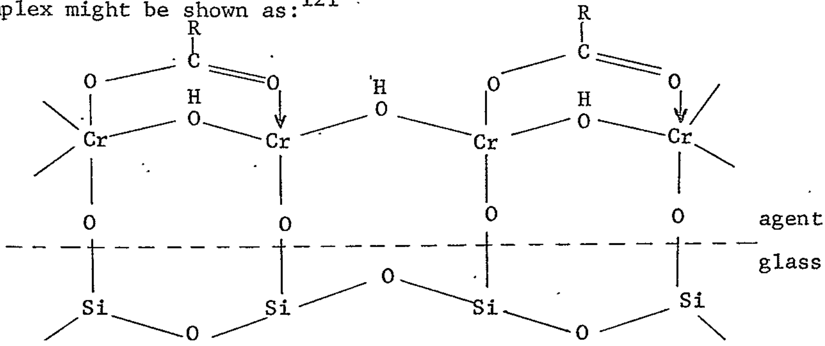
Dilution with water, particularly within pH ranges from 5 to 7, begins hydrolysis in which some chloride ions are replaced by hydroxyl groups as shown below:[343]



As hydrolysis continues, polymerization begins by the process of olation whereby the complexes are connected by hydroxyl groups:



Olation continues with a resulting increase in the size and positive charge of the complex. Absorption of the complex by a substrate surface may occur at any time in the olation process and is thought to occur at negatively charged sites on the surface. Thus, acidic positions such as SiOH in glass will attract the complex if the pH is high enough to encourage ionization to SiO^-. The pH necessary for effective coupling varies with the type of glass due to variation in ionization of acid groups with glass composition. The bond between a glass surface and the complex might be shown as:[121]



Interaction of the chromium complex with the adhesive is of three types:[343]

(a) Coordinate covalent bonding between carboxyl, alcohol, and amine end groups.

(b) Reactions between Cr-Cl and CrOH groups with alcohol end groups to form Cr-O-R linkages with the elimination of either HCl or H_2O.

(c) Copolymerization between the double bonds of methacrylic acid and reactive vinyl type double bonds in the resin.

Interaction of types (a) and (c) depend largely on the type of acid used in making the complex. The acids can be broadly classified as having reactive or non-reactive R̲ groups. Reactive R̲ groups are unsaturated (for copolymerization) or contain functional groups capable of participating in hydrogen bonding. In addition to methacrylic, acrylic,[337] phthalic,[3] and succinic acids[230] have been used as "reactive" complexing acids.

"Nonreactive" acids are exemplified by stearic acid which is used principally to impart a hydrophobic finish to surfaces[166] and does not aid adhesion of glass to polyester resins.[121] However, stearic acid-chromium complexes are useful in treating $CaCO_3$ filler for such resins. Complexes of several carboxylic acids, saturated and unsaturated, mono- and dibasic, were evaluated for effectiveness in the surface treatment of $CaCO_3$ filler for absorption of polyester resins, and caproic acid was found to be superior.[2]

Chromium complexes have been used mainly to treat glass surfaces with only limited application to other substrates. Application is made by dipping the glass surface in a dilute aqueous solution of the acid-chromic chloride complex whose pH is maintained near 6. Aging of the complex to allow olation and polymerization has been shown to greatly improve performance as a coupling agent. The surface is then dried at ~150°C prior to the addition of the adhesive polymer. (An exception in which

6

no adhesive is used is a novel method of preparing inner-reflecting glass spheres by dropping hot spheres into a cold solution of methacrylato-chromic chloride. The complex is the bonding agent which holds the fractured spheres together.[339])

Other substrates to which chromium complexes have been applied include cellulose,[100] mineral fibers,[78b] rubber,[69] leather and textiles.[3, 166] Cellulose and mineral fibers were treated to increase their adherence to polyolefin films. Rubber was given increased moisture resistance by treatment prior to vulcanization. Hydrophobic finishes were imparted to leather, paper, and other textiles by treatment with a stearic or oleic acid complex. A related process involves addition of chromium salts to polyvinyl alcohol and polyacrylic acid to increase their elasticity, water resistance and film-forming capacity.[230]

Chromium complexes have been used as adhesion promoters with a variety of adhesives. Epoxy resins have been widely used in joining treated glass surfaces,[109, 131, 227] in bonding treated mica in electrical insulators,[149] and in moldings with treated SiO_2 filler.[252]

Polyester adhesives have been used to bond treated glass surfaces.[1, 126, 129, 216, 275, 334] Chromium-complex-treated sand filler has been molded with polyester resin to produce stain-resistant cast-resin surfaces.[51] Combinations of polyester and epoxy resins have been used on treated glass laminates[8] and in molding treated mica filler.[149]

Phenolic resins have been used to laminate glass fibers which had been previously treated with methacrylato-chromic chloride.[44, 129] Phenolic, epoxy, polyester, and organo silicon resins were tested alone and in combinations for adhesion to treated glass surfaces[109] where epoxy resins were found to be superior.

Several investigations[27, 126, 129, 131, 275] have compared the efficiency of chromium complexes and silanes in promoting adhesion of glass substrates to various adhesives. The silanes were always found to be superior particularly with polyester adhesives.

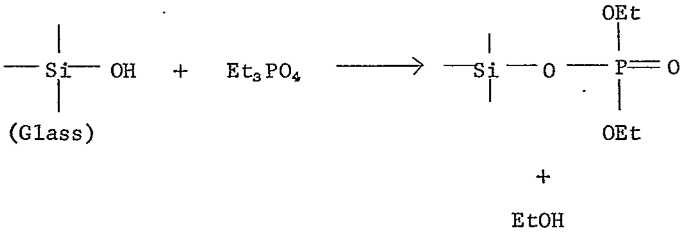
While chromium complex coupling agents increase dry bond strengths significantly, their real value is in increasing wet strength or moisture resistance of bonds.. For instance, dry strength of glass-epoxy laminate was increased by 30% while wet strength was increased by 100% over that of the untreated substrate.[67] However, in one case[27] methacrylic acid-chromium complex treated glass was found to have poorer resistance to water absorption that untreated glass when bonded with polyester. These poor results are attributed to experimental and handling techniques, since improvement in wet strength is obtained if the Cl/Cr mole ratio is between 0.1 - 1.2 (optimum 0.6 - 0.7) when the methacrylato-chromium complex is prepared. The Cl/Cr ratio is adjusted by varying the amount of CrO_3 and HCl added to methacrylic acid.[307]

IV. PHOSPHORUS CONTAINING COMPOUNDS

Some phosphorus compounds are known to behave as coupling agents. Esters of phosphoric, phosphonic, and phosphorous acids react with epoxy resins and decrease their viscosities.[133] Wollastonite, when treated with H_3PO_3 before addition to a polyester containing tritolyl phosphate (TTP), contributes significantly to the flexural strength of the filled material.[206] In place of TTP one can utilize phosphate esters substituted with allylic, vinyl, ester, and amino alkyl groups. It is postulated that the mineral filler is bonded to the polymeric matrix by virtue of a phosphorus linkage.

A considerable amount of definitive work has been done with these phosphorus agents at the Naval Applied Science Laboratory b Schrader, Lerner, D'Oria and Deutsch.[263, 264, 265, 266, 267, 268] Triethylphosphate was found to adsorb irreversibly on E glass surfaces in a high vacuum system. Desorption/decomposition experiments at high temperatures indicated the original adsorption mechanisms to be:

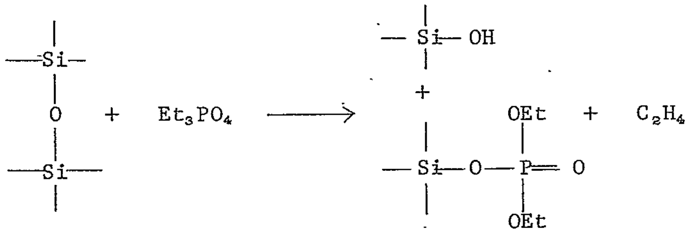
(1)



$$-\underset{(Glass)}{\overset{|}{\underset{|}{Si}}}-OH + Et_3PO_4 \longrightarrow -\overset{|}{\underset{|}{Si}}-O-\overset{OEt}{\underset{OEt}{P}}=O + EtOH$$

and

(2)



$$\equiv Si-O-Si\equiv + Et_3PO_4 \longrightarrow \equiv Si-OH + \equiv Si-O-P(=O)(OEt)_2 + C_2H_4$$

Such treatments once again showed improved flexural strengths when used on E glass cloth in epoxy laminates.[266]

Next, a study with TTP labeled with ^{32}P and ^{14}C showed two reactions to occur at the surface: (1) the formation of a primary chemical bond, Si-O-P, between TTP and the glass surface; and (2) hydrolysis of TTP by adsorbed water to give cresol and H_3PO_4,[265] which contributes to De Lollis' desorption mechanism.[76a] Further tracer studies showed a three-component film present upon adsorption of diethyl phosphite (DEP): (1) a water soluble material at 25°C which is physically adsorbed, (2) a species chemisorbed through a single Si-O-P bond which is insoluble in water at 25°C, and (3) a water insoluble portion at 100°C which is bonded through multiple Si-O-P bonds. The physically adsorbed layer is believed to participate in increasing the dry strength of epoxy laminates.[264] The general method for applying DEP to glass is to place the substrate in a 1% aqueous solution of DEP, air dry, and heat at 150°C for 10 minutes.[263]

Similar multi-component films were found with ^{14}C labeled (γ-aminopropyl)-triethoxysilane (A-1100).[267] An increase in the temperature of adsorption of these agents increases the stability (irreversibility) of the layer. This effect is due to the fact that at higher temperature, a polymeric monolayer is formed with multiple sites of attachment to the surface.[268] Thus, when one surface bond is reversibly broken by hydrolysis it has time to reform before other functions are hydrolyzed. This is the same synergistic effect experienced by Hackerman and coworkers[11, 97b, 115b] when studying polymeric piperidinyl corrosion inhibitors. They noticed an increase in corrosion inhibition (by chemisorption) by four orders of magnitude when the degree of polymerization of the adsorbed species was greater than four.

Organophosphorus compounds have also shown utility in increasing the adhesion of polymeric substrates to metals and other organic adhesive systems. Thus, radiation grafting of $(ClCH_2CH_2O)_2\ P(O)CH{:}CH_2$ to polypropylene improves its adhesion to metals with only a small change in bulk properties.[179] This method also allows the study of interfacial effects independent of the bulk properties. This same study claims that interfacial effects act only up to a critical minimum value above which the bulk mechanical properties of the adhesive are the sole determinants of total strength. This contributes to the observation of the high strengths obtained when one can achieve cohesive failure.

Similarly, ethylene-vinyl acetate copolymers show increased adhesion to metals when they are peroxide crosslinked in the presence of trialkylphosphate, where the alkyl groups are incorporated into the backbone leaving pendant phosphate moieties.[67]

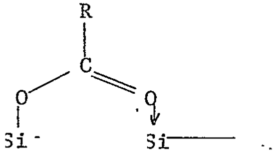
Thermoplastic solution adhesives containing TTP are used for bonding PVC to aluminum, steel to zinc, and for ABS to aluminum.[5]

Even fluorinated polyolefins show adhesive improvements on treatment with phosphites. Dipping poly(trifluorochloroethylene) in dibutyl phosphite at 150°C allows it to be bonded to an acrylate-acrylic acid copolymer sheet under pressure.[68] The mechanism in this case may be different than with metallic substrates in that here a transesterification of the surface phosphite may be the bonding mode.

V. MISCELLANEOUS AGENTS

A. Acids

Several different types of carboxylic acids have been used as coupling agents on metals, glass, and other substrates. The polar carboxyl group has the capability of coordinating or reacting with polar surface groups such as the SiOH of glass or the AlOH of aluminum in much the same fashion as do chromium complexes or phosphorous compounds:



Probably the stability of this complex is reduced because of the fewer coordinating positions of the carboxyl group relative to the chromium or phosphorous compounds. The presence of an *ortho*-hydroxyl or thiol group in the more effective salicylic[137, 177] and thiosalicylic acids[231] offers the possibility of a third coordinating position which would increase stability. Salicylic acid has been incorporated into a phenolic resin to form an adhesive which is effective on a wide variety of substrates.[177] Salicylic acid has also been used as a pretreatment of glass for resin adherence[137] and thio-salicylic acid as a pretreatment of cord fabric to increase rubber adhesion.[231]

The carbon chain, R, has been varied considerably in the evaluation of coupling effectiveness of acids. The same concepts apply to the R groups of the acids as to those of the silanes and chromium complexes, and the group may be reactive or nonreactive toward the adhesive resin. The seventeen-carbon saturated R-group of stearic acid exemplifies the nonreactive type. It has been shown to increase the bond strength of metals bonded with polyvinyl-formal-phenol resin by 5-500% if applied as a 0.02-0.06% part of the resin, whereas higher concentrations weakened the bond.[215]

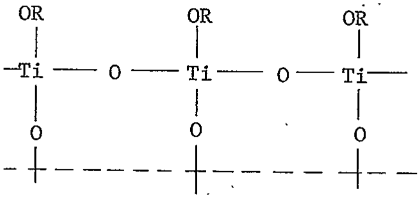
Other investigators have shown the value of a mono-molecular layer of the acid applied to the substrate. Application has been made either by carefully dipping the substrate in water which is covered by a monolayer of stearic acid[10] or by electrophoresis.[255] Stearic acid has been shown to greatly improve the moisture resistance of polyethylene bonds between treated aluminum plates.[10, 62, 324a]

The extraordinary effectiveness of the p-chlorophenyl group as the terminal substituent of R groups in increasing adhesion is attributed to the relatively high-energy chlorophenyl outer surface exposed to the adhesive resin, thus producing a surface which is easily wet by the adhesive. The p-chlorophenyl moiety has been used as a terminal substituent on 12, 14, 18 and 20-carbon carboxylic acids and as an ethyl silane substituent.[18, 225, 273]

Acids with reactive R groups, such as maleimidopropionic or succinimidopropionic, have been used as coupling agents on several metals and alloys for epoxy bonding. Aluminum bonded in this manner showed good resistance to boiling water for 48 hours.[274] Incorporation of unsaturated acids into the backbone of the polymer chain has been shown to be an effective way of increasing the adherence of the polymer to polar surfaces. The concentration of acid must be kept low to prevent association between the carboxyl groups which reduces surface adherence.[53, 143]

B. Titanates

Increasingly of late, tetra esters of orthotitanic acid have been mentioned as coupling agents for glass, metals, and polymers. While no published mechanism for their action was found, it can be postulated that some of the ester linkages are hydrolyzed and coordination or condensation occurs between the resulting hydroxyl groups and surface groups. Furthermore, polymerization between adjacent titanate groups is likely, considering the effectiveness of poly(dialkyl titanates) as coupling agents.[133] Thus the interface between a polar surface and a titanate coupling agent might be pictured as:



The choice of alkoxy groups on the titanate determines the rate of hydrolysis, which has been reported to be the critical factor in proper surface preparation.[112] Butyl and isopropyl groups are the most widely used.

Alkyl titanates are also effective coupling agents for polyethylenes,[112, 113, 150] and interaction with such a non-polar surface is more difficult to envision. In any event, at least one alkoxy or hydroxy group is available for interaction with the adhesive resin by dipolar attraction or reaction. In addition to polyolefins, polyesters also benefit from titanate treatment prior to coating with polyethylene.[37, 43]

Aluminum, copper, and steel have been treated with a 'primer' composed of an amino silane mixed with tetraisopropyl titanate before bonding with a silicone adhesive.[95] Copper showed the greatest improvement in bond strength. A similar mixture of silane-titanate has been incorporated into polymers (vinyl, epoxy, or ester) for coating glass fibers.[254] Titanium chelates such as titanium acetyl acetonate, were also used in place of the tetra ester. Use of the chelates on glass surfaces has been investigated by equilibrium studies and the possibility has been raised of acidic surface sites catalyzing both the chelate hydrolysis and subsequent condensation with the surface silanol groups.[344]

C. Amines

Amines have been used to a limited extent as coupling agents. Quaternary ammonium salts, which exhibit a positively charged nitrogen to bond with nucleophilic surface positions, have been used to increase adhesion of resins to glass.[39] A salt having at least one long-chain hydrocarbon radical is used to pretreat the glass surface.

Polyester films and fabrics show excellent adhesion to rubber if they are treated prior to vulcanization with a diamine such as 1,2-diaminoethane. Tear strength was increased forty fold over untreated polyesters.[316]

The effectiveness of certain amines in preventing aqueous corrosion of steel surfaces has promoted interest in their use as coupling agents. Amines have been shown to be chemisorbed in a mono-layer on the steel by virtue of the unbonded pair of electrons on the nitrogen and the vacant 'd' shell of iron.[12, 97b, 115b] Four-ethyl piperidine, which is particularly well adsorbed because of favorable polar and steric factors, bonds through the nitrogen atom and thus exposes the ethyl group for interaction with an adhesive resin. Further investigation is needed to determine optimum concentrations, substituent groups, substrates and adhesives to utilize piperidine coupling, although 4-aminomethylpiperidine has been shown to be beneficial in steel-epoxy systems.[54b]

VI. COMMERCIALLY AVAILABLE AGENTS

The following table is a compilation of commercially available coupling agents and their suppliers along with an elucidation of their structures. The list is divided along the same major lines as the entire paper, e.g., silanes, chromium complexes, and phosphorous compounds with appropriate subdivisions.

It should be noted that several of these compounds, particularly in the phosphorous section, are not marketed as coupling agents; however, since this review of the literature has found evidence that these types of compounds can be effective coupling agents, they are included in the compilation.

This collection is not meant to be complete with respect to commercial sources but presents a comprehensive list of types available.

TABLE I

COMMERCIALLY AVAILABLE COUPLING AGENTS

Silanes $R-SiX_3$ (X = hydrolyzable group)

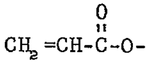
A. Saturated alkyl and haloalkyl R group

1. Methyltrichloro silane, CH_3SiCl_3 (General Electric S.C.-3100 and Stauffer SWS-442)
2. Ethyltriethoxy silane, $CH_3-CH_2-Si(OEt)_3$ (General Electric SC-3735)
3. γ-Chloropropyltrimethoxy silane, $Cl-CH_2-CH_2-CH_2-Si(OCH_3)_3$ (Dow Corning Z-8-0999)
4. Dimethyldichloro silane, $(CH_3)_2SiCl_2$ (Stauffer SWS-441)

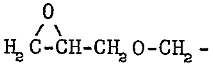
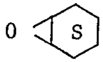
B. Aryl and haloaryl R group

1. Phenyltrimethoxy silane, $C_6H_5-Si(OCH_3)_3$ (Dow Corning 6071)
2. p-Chlorophenyltrichloro silane, $Cl-C_6H_4-SiCl_3$ (K&K 13181)

C. Unsaturated alkyl R group

1. Vinyltriethoxy silane, $CH_2{=}CH-Si(OEt)_3$ (Union Carbide A-151 and Dow Corning Z-6075)
2. γ-Methacryloxypropyltrimethoxy silane,  $CH_2{=}CH-\overset{\overset{O}{\|}}{C}-O-CH_2CH_2CH_2-Si(OCH_3)_3$ (Union Carbide A-174 and Dow Corning Z-6030)

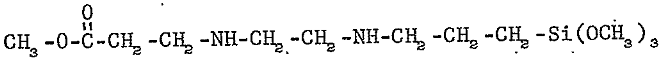
D. Epoxy R groups

1. γ-Glycidoxypropyltrimethoxy silane,  $H_2\overset{O}{\widehat{C-CH}}-CH_2O-CH_2-CH_2-CH_2-Si(OCH_3)_3$ (Dow Corning A-6040 and Union Carbide A-187)
2. β-(3,4-Epoxycyclohexyl)-ethyltrimethoxy silane,  $-CH_2CH_2-Si(OCH_3)_3$ (Union Carbide A-186)

E. Amino R group

1. γ-Aminopropyltriethoxy silane, $H_2N-CH_2-CH_2-CH_2-Si(OEt)_3$ (Union Carbide A-1100)

2. N-β-(Aminoethyl)-γ-aminopropyltrimethoxy silane, $H_2N-CH_2-CH_2-NH-CH_2-CH_2-CH_2-Si(OCH_3)_3$ (Union Carbide A-1120 and Dow Corning Z-6020)

3. 
$CH_3-O-\overset{\overset{O}{\|}}{C}-CH_2-CH_2-NH-CH_2-CH_2-NH-CH_2-CH_2-CH_2-Si(OCH_3)_3$
(Dow Dorning C-600)

F. Mercapto R group

γ-Mercaptopropyltrimethoxy silane, $HS-CH_2-CH_2-CH_2-Si(OMe)_3$ (Union Carbide A-189)

II. Chromium Complexes (Acid Functions - Given)

A. Methacrylo, $H_2C{=}C(CH_3)-CO_2-$ (Dupont-Volan)

B. Stearo, $CH_3(CH_2)_{16}-CO_2-$ (Valchem--Valchrome 5015)

III. Tetra-alkyl Titanates $(R-O)_4Ti$ (R-O Groups Given)

A. Isopropyl, $(CH_3)_2CH-O-$ (Stauffer)

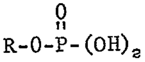
B. n-Butyl, $CH_3-(CH_2)_3-O-$ (Stauffer)

C. 2-ethylhexyl, $CH_3-(CH_2)_3-CH(CH_2-CH_3)-CH_2-O-$ (Stauffer)

D. Cresyl, $CH_3-C_6H_4-O-$ (Stauffer)

IV. Phosphorous Compounds (R Groups Given)

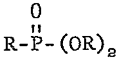
A. Phosphates

1. Monoalkyl acids 
$R-O-\overset{\overset{O}{\|}}{P}-(OH)_2$

   a. Butyl (Stauffer and Mobil)

   b. Ethyl (Stauffer and Mobil)

   c. Isoamyl (Stauffer and Mobil)

B. Phosphonates  $R-\overset{\overset{O}{\|}}{P}-(OR)_2$

   1. Diphenylphenyl (Stauffer)
   2. Dimethylmethyl (Mobil)
   3. Diethylethyl (Mobil)
   4. <u>Bis</u>-(2-ethylhexyl)-2 ethylhexyl (Mobil)
   5. Dibutylbutyl (Mobil)

C. Phosphites $(R-O)_2P-OH$

   1. Dimethyl (Stauffer)
   2. Diethyl (Stauffer)
   3. di-isopropyl (Stauffer)
   4. Dioctyl (Stauffer)
   5. Weslink E (Weston Chemical Co.) (exact structure unavailable)

VII. EVALUATION DATA

Most of the preceding discussion of the effectiveness of coupling agents in increasing dry and wet adhesive strength has been in qualitative terms. Some quantitative tests have been conducted but direct comparison between reported values is difficult because conditions were varied considerably. However, some of the reported data were selected for presentation in Table II to convey some insight into the adhesion-enhancing ability of the coupling agents. Items were chosen to represent as wide a variety of coupling agents, adhesives, substrates, and test conditions as possible from the available data. Bond improvement is reported as the ratio of bond strength with coupling agent to bond strength without coupling agent.

TABLE II

QUANTITATIVE EVALUATION OF COUPLING AGENT EFFECTIVENESS

Type	R-Group	Adhesive	Substrate	Test Type	Test Conditions	Bond Improvement (Treated/Untreated)	Reference
Silanes R-SiX$_3$	α-amino propyl	poly olefin	glass-rubber	peel strength	dry	7.8	65
	α-amino propyl	epoxy-phenolic	glass laminate	tensile strength	dry	1.3	110
					2 hours boiling water	1.6	
	vinyl	polyester	glass laminate	flex strength	dry	1.3	162
					2 hours boiling water	3.0	
	methyl methacrylate	polyester	glass laminate	flex strength	dry	1.4	162
					2 hours boiling water	4.2	
	3-glycidoxy propyl	polyester	glass laminate	adhesive strength	dry	1.4	228
	3,4-epoxy cyclohexyl ethyl	polyester	glass laminate	adhesive strength	dry	1.2	228
	p-cyanophenyl	polybenzimidiazole	glass laminate	flex strength	dry	1.4	240
					2 hours boiling water	1.4	
	mercapto propyl	phenolic-acrylonitrile	aluminum	lap shear	73°F	2.1	244
					250°F	3.3	244
	amino propyl	phenolic-acrylonitrile	aluminum	lap shear	73°F	1.6	244
					250°F	2.3	244
	3-glycidoxyl propyl	polyurethane	aluminum	lap shear	75°F	1.7	304
					-300°F	1.3	304
					+200°F	4.4	304
Chromium Complex	methacrylic acid	polyester	glass laminate	flex strength	dry	1.3	121
					3 hours boiling wate	1.7	
	trihydroxybenzoic	epoxy	glass laminate	flex strength	dry	1.2	121
					100 hours boiling water	2.2	
Carboxylic Acid R - CO$_2$H	salicylic	chloroprene-neoprene copolymer	canvas	peel strength	100°F	1.6	177
					200°F	1.7	
	succinimido-acetic	epoxy	aluminum	shear strength	dry	1.6	274
					48 hours boiling water	$\left(\frac{2000}{0}\right)$	

VIII. ACKNOWLEDGMENTS

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A. BIBLIOGRAPHY OF ARTICLES

1. Aber, Jesse I., U. S. Patent 3,262,809 (July 1966); Chem. Abstr., 65, 13889g (1966); 4, 7, 14, 22.
2. Akita, Tsutomu and Naomi Kurihara, Reinforced Plastics, 4, 2-5 (1958); Chem. Abstr., 53, 1809h (1959); 4, 22, 25, 34.
3. Aktiebolaget, S. O. Brit. Patent 788,539 (Jan. 1958); Chem. Abstr., 52, 13796e (1958); 7, 17, 22.
4. Alksne, V. I., K. P. Grinevich, and I. E. Yakobson, Foreign Technology Divs., Wright-Patterson AFB, Ohio, Rept. No. FTD-HT-23-682-68, (7 Nov. 1968); USGRDR, 69(5), 124 (1969); 4, 14, 16, 24, 31.
5. Aluminum francais, Fr. Patent 1,192,267 (Oct. 1959); Chem. Abstr., 54, 26021c (1960); 4, 12, 13, 16, 17, 21.
6. American Cyanamid Co., Neth. Appl. Patent 6,508,268, (Jan. 1966); Chem. Abstr., 64, 19922d (1966); 2, 13, 24, 31.
7. American Cyanamid Co., Neth. Appl. Patent 6,605,081, (Oct. 1966); Chem. Abstr., 66, 66168e (1967); 2, 17, 24.
8. Andreevskaya, G. D., Yu. A. Gorbatkina, A. V. Zamotova, R. L. Kiseleva, T. V. Odnoletkova, and R. Ya. Khvitivitskii, Mekhan. Polimerov, Akad. Nauk Latv. SSR (1965); Chem. Abstr., 63, 1938h (1965); 1, 4, 14, 22, 24, 25.
9. Andreevskaya, G. D., Yu. A. Gorbatkina, N. B. Guseva, B. A. Kiselev, A. I. Mikhal'skii, and V. N. Stepanova, Vysokomolekul. Soedin., 7(7), 1254-7 (1965); Chem. Abstr., 63, 10123b (1965); 5, 14, 24.
10. Anon., Plastics Technol., 9, No. 2, 11-13 (1963); Chem. Abstr., 58, 9287b (1963); 7, 12, 16, 17, 25.
11. Armistead, C. G., and J. A. Hockey, Trans. Faraday Soc., 63 (10), 2549-56 (1967); Chem. Abstr., 67, 103088x (1967); 14, 24, 32.
12. Annand, R. R., R. M. Hurd, and Norman Hackerman, J. Electrochem. Soc., 112 (2), 138-44 (1965); Chem. Abstr., 62, 6208h (1965); 13, 23, 32.
13. Aslanova, M. S., Plasticheskie Massy, 8, 31-3 (1960); Chem. Abstr., 55, 13797c (1961); 7, 14, 16, 25, 32, 33.

14. Aslanova, M. S., Verres Refractaires, 19(2), 107-12 (1965); Chem. Abstr., 63, 6693b (1965); 14, 32.

15. Atwell, Everett C., U.S. Patent 3,318,757 (May 1967); Chem. Abstr., 67, 22561u (1967); 7, 14, 16, 24.

16. BTR Industries Ltd., Fr. Patent 1,356,819 (Mar. 1964); Chem. Abstr., 62, 4220a (1965); 14, 21, 22, 24, 25.

17. Babich, V. F. Ya. D. Avrasin, and A. L. Rabinovich, Fiz.-Khim. Mekh. Orientirovannykh Stekloplast, 144-9 (1965); Chem. Abstr., 68, 78975v (1968); 1, 24, 32.

18. Baier, R. E., Elaine G. Shafrin, and William A. Zisman, Science, 162(3860), 1360-8 (1968); Chem. Abstr., 70, 48284t (1969); 32, 33.

19. Baigozhin, A., and L. V. Sergeev, Vysokomolekul. Soedin., 4, 972-6 (1962); Chem. Abstr., 59, 807g (1963); 4, 14, 24.

20. Baigozhin, A., L. V. Sergeev, A. K. Dabagova, and S. G. Fattakhov., Vysokomolekul. Soedin., 75-8 (1963); Chem. Abstr., 60, 9422h (1964); 7, 14, 24, 32.

21. Barenholtz, George J., I. C. Chu, and John E. Rutzler, Jr., Am. Chem. Soc. Div. Paint, Plastics, Printing Ink, Chem., Preprints, 20, No. 1, 117-23 (1960); Chem. Abstr., 57, 6120d (1962); 1, 12, 32, 34.

22. Barenholtz, George J., John E. Rutzler, Jr., and E. G. Bobalek Ind. Eng. Chem., Prod. Res. Develop., 2(4) 270-2 (1963); Chem. Abstr., 59, 15436g (1963); 1, 13, 31, 32.

23. Barenholtz, George J., and John E. Rutzler, Jr., Am. Chem. Soc., Div. Org. Coatings Plastics Chem., Preprints, 22(1), 223-39 (1962); Chem. Abstr., 59, 12982c (1963); 1, 13, 31, 32.

24. Barnet, F. R., and J. Cuevas, Mod. Plast. 44(4), 161-205 (1966); Chem. Abstr., 66, 38373z (1967); 1, 14, 16, 24, 34.

25. Barnet, Robert, and J. Cuevas, Proc., Ann. Tech. Conf., SPI, (1966); Chem. Abstr., 65, 15600 (1966); 1, 14, 17, 32, 34.

26. Barry, Arthur J., U.S. Patent 2,557,778 (June 1969); Chem. Abstr., 45, 8288g (1951); 3, 6, 14, 15, 24.

27. Barthel, R., H. Gocke, and C. M. Hiller, Plaste Kaut., 14(12), 894-8 (1967); Chem. Abstr., 68, 78990w (1968); 4, 5, 7, 14, 15, 24.

28. Barton, E. E., Plastics Inst. Trans., 18, 1-21 (1950); Chem. Abstr., 45, 4479d (1951); 5, 13, 34, 35.

14. Aslanova, M. S., Verres Refractaires, 19(2), 107-12 (1965); Chem. Abstr., 63, 6693b (1965); 14, 32.

15. Atwell, Everett C., U.S. Patent 3,318,757 (May 1967); Chem. Abstr., 67, 22561u (1967); 7, 14, 16, 24.

16. BTR Industries Ltd., Fr. Patent 1,356,819 (Mar. 1964); Chem. Abstr., 62, 4220a (1965); 14, 21, 22, 24, 25.

17. Babich, V. F. Ya. D. Avrasin, and A. L. Rabinovich, Fiz.-Khim. Mekh. Orientirovannykh Stekloplast, 144-9 (1965); Chem. Abstr., 68, 78975v (1968); 1, 24, 32.

18. Baier, R. E., Elaine G. Shafrin, and William A. Zisman, Science, 162(3860), 1360-8 (1968); Chem. Abstr., 70, 48284t (1969); 32, 33.

19. Baigozhin, A., and L. V. Sergeev, Vysokomolekul. Soedin., 4, 972-6 (1962); Chem. Abstr., 59, 807g (1963); 4, 14, 24.

20. Baigozhin, A., L. V. Sergeev, A. K. Dabagova, and S. G. Fattakhov., Vysokomolekul. Soedin., 75-8 (1963); Chem. Abstr., 60, 9422h (1964); 7, 14, 24, 32.

21. Barenholtz, George J., I. C. Chu, and John E. Rutzler, Jr., Am. Chem. Soc. Div. Paint, Plastics, Printing Ink, Chem Preprints, 20, No. 1, 117-23 (1960); Chem. Abstr., 57, 6120d (1962); 1, 12, 32, 34.

22. Barenholtz, George J., John E. Rutzler, Jr., and E. G. Bobalek, Ind. Eng. Chem., Prod. Res. Develop., 2(4) 270-2 (1963); Chem. Abstr., 59, 15436g (1963); 1, 13, 31, 32.

23. Barenholtz, George J., and John E. Rutzler, Jr., Am. Chem. Soc., Div. Org. Coatings Plastics Chem., Preprints, 22(1), 223-39 (1962); Chem. Abstr., 59, 12982c (1963); 1, 13, 31, 32.

24. Barnet, F. R., and J. Cuevas, Mod. Plast. 44(4), 161-205 (1966); Chem. Abstr., 66, 38373z (1967); 1, 14, 16, 24, 34.

25. Barnet, Robert, and J. Cuevas, Proc., Ann. Tech. Conf., SPI, (1966); Chem. Abstr., 65, 15600 (1966); 1, 14, 17, 32, 34.

26. Barry, Arthur J., U.S. Patent 2,557,778 (June 1969); Chem. Abstr., 45, 8288g (1951); 3, 6, 14, 15, 24.

27. Barthel, R., H. Gocke, and C. M. Hiller, Plaste Kaut., 14(12), 894-8 (1967); Chem. Abstr., 68, 78990w (1968); 4, 5, 7, 14, 15, 24.

28. Barton, E. E., Plastics Inst. Trans., 18, 1-21 (1950); Chem. Abstr., 45, 4479d (1951); 5, 13, 34, 35.

29. Bascom, W. D., Laura A. Halper, and N. L. Jarvis, I&EC Product Research and Development, 8(2), 118-123 (1969); 13,16,24,25,32.

30. Becker, Robert, Adolf Gesierich, and Alfred Wende, Ger. Patent 58,348 (Oct. 1967); Chem. Abstr., 69, 52717h (1968); 1, 13, 17, 24, 31.

31. Becker, Robert, Adolf Gesierich, Alfred Wende, and Guenter Walter, Ger. Patent 54,049 (Feb. 1967); Chem. Abstr., 68, 69866h (1968); 1, 14, 24, 34.

32. Becker, Robert, Adolf Gesierich, Guenter Walter, and Alfred Wende, Ger. Patent 41,469 (Sept. 1965); Chem. Abstr., 64, 8419f (1966); 1, 14, 17, 24.

33. Becker, Robert, Adolf Gesierich, A. Walter, and Alfred Wende, Plaste Kaut. 14(2), 96-8 (1967); Chem. Abstr., 66, 66244b (1967); 1, 14, 24.

34. Becker, Robert, Adolf Gesierich, Ingrid Schweitzer, and A. Wende, Plaste Kaut., 14(6), 406-8 (1967); Chem. Abstr., 67, 44467v (1967); 1, 6, 14, 24, 34.

35. Becker, Robert, Plaste Kaut., 14(11), 833 (1967); Chem. Abstr., 68, 69625 (1968); 1, 16, 17, 24.

36. Becker, Robert, Adolf Gesierich, and Alfred Wende, Silikattechnik, 19(6), 184-7 (1968); Chem. Abstr., 69, 79819e (1968); 1, 14, 24.

37. Blatz, Philip, U.S. Patent 3,057,753 (Oct. 1962); Chem. Abstr., 58, 3576e (1963); 4, 16, 25.

38. Bock, Eugen, Angew. Makromol. Chem., (4/5), 116-41 (1968); Chem. Abstr., 70, 205469f (1969); 2, 3, 15, 32.

39. Bollinger, Wilhelm, and Wilhelm Langer, Ger. Patent 1,285,694 (Dec. 1968); Chem. Abstr., 70, 69353e (1969); 7, 14, 25.

40. Boyer, William M, Hyman M. Molotsky, and Harlan E. Tarbell, Jr., U.S. Patent 3,038,875 (June 1962); Chem. Abstr., 57, 7413c (1962); 1, 6, 24.

41. Brewis, Derek M., Polym. Eng. Sci., 7(1), 17-20 (1967); Chem. Abstr., 66, 46715c (1967); 1, 7, 17, 32.

42. Brill, Harold C., U.S. Patent 2,943,955 (July 1960); Chem. Abstr., 55, 2202h (1961); 12, 13, 14, 16, 25.

43. Brill, Harold C., U. S. Patent 3,002,854 (Appl. Apr. 1957); Chem. Abstr., 56, 1622i (1962); 4, 12, 16, 25, 31.

44. Bronshtein, Z. I., Yu. V. Meitin, F. S. Smel'nitskii, A. M. Voronova, and V. A. Murav'ev, Plasticheskie Massy (10), 59-63 (1965); Chem. Abstr., 63, 18361c (1965); 5, 14, 22, 24.

45. Brooks, Marvin C., U. S. Patent 2,754,237 (July 1956); Chem. Abstr., 50, 16183f (1956); 4, 14, 24.

46. Brooks, Marvin C., U. S. Patent 2,885,383 (May 1959); Chem. Abstr., 53, 15651d (1959); 4, 14, 24, 31.

47. Brooks, Marvin C., U.S. Patent 2,891,885 (June 1959); Chem. Abstr., 53, 19453t (1959); 4, 14, 24.

48. Broutman, Lawrence J., Polymer Eng. Sci., 6(3), 263-72 (1966) Chem. Abstr., 65, 10738g (1966); 1, 4, 14, 25, 33.

49. Bueche, Arthur M., and Curtis S. Oliver, U. S. Patent 3,024,146 (Mar. 1962); Chem. Abstr., 57, 1098a (1962); 6, 12, 24, 31.

50. Bueche, Arthur M., and Curtis S. Oliver, U. S. Patent 3,031,366 (Apr. 1962); Chem. Abstr., 57, 4890e (1962); 6, 12, 24, 34.

51. Burns & Russell Co., Brit. Patent 966,864 (Aug. 1964); Chem. Abstr., 62, 1800a (1965); 4, 17, 22, 24.

52. Burushkina, T. N., A. A. Chuiko, N. V. Khaber, and L. V. Manchenko, Teor. Eksp. Khim., 4(4), 570-2 (1968); Chem. Abstr., 69, 99760g (1968); 24, 32.

53. Busse, Warren F., and John A. Boxler, U. S. Patent 2,838,437 (June 1958); Chem. Abstr., 52, 17814i (1958); 7, 25.

54a. Carlstrom, B. I., and P. T. Agren, Swed. Patent 198,775 (Oct. 1965); Chem. Abstr., 64, 9180e (1966); 6, 14, 22, 24.

54b. Cassidy, P. E., G. C. Rolls and J. M. Johnson, TRACOR, Inc., Unpublished data, NASA Contract NAS8-24073.

54c. Cassidy, P. E. and Feith, K. E., TRACOR Document Number 69-502-C, 16 May 1969, Contract N00024-68-C-1227.

55. Chadha, Rajendra N., Fr. Patent 1,503,341 (Nov. 1967); Chem. Abstr., 69, 87881j (1968); 6, 16, 17, 24.

56. Ch'eng, Chi-Chien, and Chih-Yao Fang, Kuei Suan Yen Hsueh Pao, 4(3), 161-70 (1965); Chem. Abstr., 64, 17220c (1966); 14, 24.

57. Chevalier, Pierre J., U. S. Patent 2,635,084 (Apr. 1953); Chem. Abstr., 47, 8413f (1953); 6, 17, 24.

58. Chi, Uyn-Shih, Hua Hsueh Tung Pao, No. 2, 97-102 (1962); Chem. Abstr., 57, 6159a (1962); 7, 14, 24, 32, 33.

59. Chuiko, A. A., V. A. Tertykh, G. E. Plavnik, and I. E. Neimark, Kolloidn. Zh., 27(6), 903-7 (1965); Chem. Abstr., 64, 6825d (1966); 14, 24, 32, 34.

60. Chuiko, A. A., and E. A. Chuiko, Sintz i Fiz.-Khim. Polimerov, Akad. Nauk Ukr. SSR, Inst. Khim. Vysokomolekul. Soedin., Sb. Statei, 83-98 (1964); Chem. Abstr., 62, 9327e (1965); 15, 24, 34.

61. Chuiko, E. A., and A. A. Chuiko, Sin. Fiz.-Khim. Polim., Akad. Nauk Ukr. SSR, Inst. Khim. Vysokomol. Soedin, 3, 129-33 (1966); Chem. Abstr., 67, 100788q (1967); 15, 24, 34.

62. Clark, H. A., and E. P. Plueddemann, Mod. Plastics, 40(10), 133-5, 137-8, 195-6 (1963); Chem. Abstr., 59, 6579a (1963); 14, 16, 24, 32.

63. Clark, H. A., and E. P. Plueddemann, Belg. Patent 616,106 (Oct. 1962); Chem. Abstr., 58, 6971e (1963); 4, 14, 24, 25.

64. Clark, H. A., U. S. Patent 2,762,717 (Sept. 1956); Chem. Abstr., 51, 3955h (1957); 4, 14, 24.

65. Clayton, Robert E., and Byron M. Vanderbilt, U. S. Patent 3,376,188 (Apr. 1968); Chem. Abstr., 68, 96664x (1968); 7, 14, 15, 24.

66. Collier, Theodore J., U. S. Patent 2,974,062 (Mar. 1961); Chem. Abstr., 55, 20519h (1961); 1, 14, 24.

67. Continental Gummi-Werke A. G., Brit. Patent 929,365 (June 1963); Chem. Abstr., 59, 8946a (1963); 7, 17, 21.

68a. Cox, Robert P., Luther L. Yaeger, and Ralph W. Buetow, U. S. Patent 2,941,912 (June 1960); Chem. Abstr., 54, 25997i (1960); 7, 16, 21, 34.

68b. Creasey, J. R., D. B. Russell, and Melvin P. Wagner, Rubber Chem. Technol., 41(5), 1300-11 (1968); Chem. Abstr., 70, 48399j, (1969); 4, 15, 17, 25.

69. Dadson, Lawrence M., U. S. Patent 2,930,715 (Mar. 1960); Chem. Abstr., 54, 15991h (1960); 15, 22.

70. Dathe, Christian, Ger. Patent 35,226 (Feb. 1965); Chem, Abstr., 63, 1956g (1965); 6, 12, 24.

71. Dathe, Christian, Ger. Patent 36,060 (May 1965); Chem. Abstr., 63, 15066c (1965); 6, 17, 24, 31.

72. Dathe, Christian, and I. Eckhardt, Plaste Kautschuk, 10(7), 404-6 (1963); Chem. Abstr., 61, 802g (1964); 6, 13, 24.

73. Davydov, A. B. and Z. G. Ivanova, Plasticheskie Massy, (1), 46-8 (1965); Chem. Abstr., 62, 7938h (1965); 16, 24, 34.

74. Dawson, William, Brit. Patent 916,865 (Jan. 1963); Chem. Abstr., 58, 11538c (1963); 14, 16, 22, 24.

75. Dean, Robert B., Offic. Dig., J. Paint Technol. Eng. 36(473) 664-78 (1964); Chem. Abstr., 62, 2879h (1965); 1, 16, 32.

76a. DeLollis, N. J., Sandia Corporation Research Report, Albuquerque, New Mexico, 68-270 (May 1968); 1, 4, 5, 6, 7, 14, 24, 31, 32.

76b. DeLollis, N. J., and O. Montoya, J. Appl. Polym. Sci., 11, 983-9 (1967); Chem. Abstr., 67, 44320s (1967); 1, 5, 7, 25, 32.

77. Deryagin, B. V., and V. Smilga, J. Appl. Phys., 38(12), 4609-16 (1967); Chem. Abstr., 68, 16400v (1968); 32.

78a. Detering, Heinz, Ger. Patent 954,456 (Dec. 1956); Chem. Abstr., 53, 13657d (1959); 1, 6, 14, 17, 24.

78b. Dickens, Peter. Klaus Gorke, Karl H. Schmidt, Conrad Kaser, and Paul König, Ger. Patent 1,052,295 (Mar. 1959); Chem. Abstr., 55, 3947d (1961); 7, 17, 22, 33.

79. Dow Corning Corp., Neth. Appl. 6,613,777 (Mar. 1967), U. S. Appl. (Sept. 1965); Chem. Abstr., 67, 91330e (1967); 6, 17, 24.

80. Dow Corning Corp., Neth. Appl. 6,600,136 (July 1966), U. S. Appl. (Jan. 1965); Chem. Abstr., 65, 20320b (1966); 14, 15, 16, 17, 24, 33.

81. Dow Corning Corp., Neth. Appl. 6,511,722 (Mar. 1966), U. S. Appl. (Sept. 1964); Chem. Abstr., 65, 4028a (1966); 6, 16, 24.

82. Dow Corning Corp., Brit. Patent 975,122 (Nov. 1964); Chem. Abstr., 62, 7948b (1965); 1, 4, 7, 14, 24, 31.

83. Dow Corning Corp., Neth. Appl. 6,402,923 (Nov. 1964), U.S. Appl. (May 1963); Chem. Abstr., 62, 10628a (1965); 7, 16, 24, 31.

84. Dow Corning Corp., Brit. Patent 1,002,795 (Aug. 1965); Chem. Abstr., 63, 18387d (1965); 5, 7, 12, 17, 24.

85. Dow Corning Product Bulletin, "Silane Coupling Agents," Dow Corning Corp., Chem. Products Div., Midland, Michigan, 48640; 1, 2, 3, 4, 5, 6, 7, 12, 13, 14, 24, 31.

86. Drisko, Richard W., Paint Varn. Prod., 58(7), 31-4 (1968); Chem. Abstr., 69, 52967g (1968); 1, 16, 17, 24, 31, 34.

87. du Pont de Nemours, E. I., & Co., Brit. Patent 1,107,419 (Mar. 1968); Chem. Abstr., 69, 3439k (1968); 1, 2, 12, 13, 16, 24.

88. du Pont de Nemours, E. I., & Co., Brit. Patent 923,382 (Apr. 1963); Chem. Abstr., 59, 8948a (1963); 1, 14, 17, 22, 31, 33.

89. Eakins, William J., U. S. Patent 3,276,853 (Oct. 1966); Chem. Abstr., 65, 18785d (1966); 14, 24.

90. Eder, Heinz, and Siegfried Bloeck, Ger. Patent 1,204,111 (Oct. 1965); Chem. Abstr., 64, 8500h (1966); 12, 24, 33.

91. Eilerman, George E., U. S. Patent 3,025,588 (Mar. 1962); Chem. Abstr., 57,1117e (1962); 3, 14, 22, 24.

92. Erickson, Porter W., NASA Accession N65-24572, Rept. No. AD 426292, (1964); Chem. Abstr., 67, 33348f (1967); 7, 14, 32.

93. Erickson, Porter W., and Irving Silver, U. S. Patent 2,776,910, (Jan. 1957); Chem. Abstr., 51, 7767g (1957); 1, 14, 24.

94. Fain, Jacob M., Edward McDonnell, and Robert Blaufox, U. S. Patent 3,244,541 (Apr. 1966); Chem. Abstr., 64, 19999f (1966); 14, 24, 33.

95. Fekete, Frank, U. S. Patent 3,321,350 (May 1967); Chem. Abstr., 67, 33645a (1967); 3, 6, 12, 13, 14, 24.

96. Fekete, Frank, U. S. Patent 3,296,182 (Jan. 1967); Chem. Abstr., 66, 56391h (1967); 6, 24, 25, 34.

97a. Fekete, Frank, Brit. Patent 887,441 (Jan. 1962); Chem. Abstr., 57, 1098d (1962); 6, 17, 24, 25.

97b. Finley, N. F. and Norman Hackerman, *J. Electrochem. Soc.*, *107*, 259 (1960); 23, 32.

98. Frank, Charles E., and Gerard Kraus, U. S. Patent 2,692,841 (Oct. 1954); *Chem. Abstr.*, *49*, 2770e (1955); 15, 17, 32, 33.

99. Franzen, Kurt, and Guenter Herkelmann, Ger. Patent 1,254,303 (Nov. 1967); *Chem. Abstr.*, *68*, 13786q (1968); 3, 5, 14, 24, 25.

100. Fujimori Kogyo Co., Ltd., Fr. Patent 1,449,532, (Aug. 1966), Japan Appl. (Oct. 1964); *Chem. Abstr.*, *66*, 96402u (1967); 7, 17, 22, 25, 33.

101. Gaehde, J., and A. Wende, *Plaste Kautschuk*, *13*(1), 23-5 (1966); *Chem. Abstr.*, *64*, 11387b (1966); 7, 14, 16, 24, 32.

102a. Gagliardi, D., Brit. Patent 1,020,052 (Feb. 1966); *Chem. Abstr.*, *64*, 16055e (1966); 17, 24, 33.

102b. General Aniline and Film Corporation, "Gantrez" product bulletin, 140 W. 51st St., New York, New York; 7, 22.

103. General Electric Co., Brit. Patent 1,091,650, (Nov. 1967); *Chem. Abstr.*, *68*, 22572u (1968); 16, 24, 33.

104. General Electric Co., Brit. Patent 825,717, (Oct. 1960); *Chem. Abstr.*, *55*, 9877d (1961); 16, 17, 24.

105. Giordano, Joseph J., Fr. Patent 1,439,853, (May 1966); *Chem. Abstr.*, *66*, 66344j (1967); 7, 12, 13, 14, 24.

106. Goldschmidt, Th., Brit. Patent 930,039, (July 1963); *Chem. Abstr.*, *59*, 14174g (1963); 14, 24, 32.

107. Golubenkova, L. I., S. N. Nikonova, A. N. Shabadash, and M. S. Akutin, *Appl. Plast.*, *10*(5), 44-6, 48-9 (1967); *Chem. Abstr.*, *67*, 33262y (1967); 1, 4, 14, 24, 32.

108. Goodwin, John T. Jr., U. S. Patent 2,857,356, (Oct. 1958); *Chem. Abstr.*, *53*, 1857e (1959); 6, 14, 16, 24.

109. Gorbatkina, Yu. A., *Plaste Kautschuk*, *13*(3), 145-50 (1966); *Chem. Abstr.*, *64*, 17796e (1966); 1, 5, 6, 7, 14, 22, 25, 33.

110. Gorbatkina, Yu. A., N. B. Guseva, G. D. Andreevskaya, and G. S. Galakhova, *Vysokomolekul. Soedin.* *6*(10), 1911-16 (1964); *Chem. Abstr.*, *62*, 2881h (1965); 1, 5, 7, 14, 24, 31.

111. Gottfurcht, Adolph, U. S. Patent 2,763,629, (Sept. 1956); *Chem. Abstr.*, *51*, 3105d (1957); 7, 14, 24.

112. Gray, C. L., Jr., W. L. MacCarthy, and T. F. McLaughlin, Modern Packaging, 34, No. 10, 143-47, 243-5 (1961); Chem. Abstr., 55, 20494h (1961); 12, 16, 25.

113. Gray, Charles J., Jr., Am. Chem. Soc., Div. Org. Coatings Plastics Chem., Preprints, 20, No. 2, 382-95 (1960); Chem. Abstr., 58, 11529g (1963); 4, 12, 16, 25.

114. Grinevich, K. P., N. N. Kryuchkov, M. V. Sobolevskii, Z. I. Bronshtein, S. N. Odisharia, M. N. Krichevskaya, and A. V. Bosomykina, U. S. S. R. Patent 144,284, (Feb. 1962); Chem. Abstr., 57, 6126d (1962); 4, 14, 24.

115a. Guivier, Hubert R., Raoul M. Joly, Fr. Patent 1,508,381, (Jan. 1968); Chem. Abstr., 70, 20641h (1969); 1, 17, 24.

115b. Hackerman, Norman, R. M. Hurd, and R. P. Annand, Corrosion, 18, 37t (1962); 23, 32.

116. Hager, Karl F., and Morris Rosenthal, U. S. Patent 2,853,412, (Sept. 1958); Chem. Abstr., 53, 1855h (1959); 6, 12, 13, 24, 31.

117. Hair, Michael L., Wm. Hertl, J. Phy. Chem., 73(7), 2372 (1969); 14, 24, 32.

118. Hamilton, Vern Edward, Luther M. Roseland, S. African Patent 67 04,865, (Jan. 1968); Chem. Abstr., 70, 38462k (1969); 1, 2, 14, 24.

119. Harper, Jack R., Fr. Patent 1,386,548, (Jan. 1965); Chem. Abstr., 63, 10173f (1965); 6, 14, 16, 17, 24.

120. Harper, Jack R., U. S. Patent 2,979,420, (Apr. 1961); Chem. Abstr., 55, 21640e (1961); 6, 12, 13, 14, 24.

121. Hauserman, F. B., Advances in Chem. Ser., 23, 338-56 (1959); Chem. Abstr., 54, 4234a (1960); 22, 29.

122. Havestadt, Ludwig, Hugo Arens, Ger. Patent 800,685, (Nov. 1950); Chem. Abstr., 45, 3142e (1951); 7, 17, 24.

123. Hazdra, James J., and Hubert M Lontz, U. S. Patent 3,341,399, (Sept. 1967); Chem. Abstr., 67, 100720m (1967); 7, 14, 24, 31.

124. Hedrick, Ross M., William R. Richard, Jr., Arthur J. Lambright, and Robert E. Miller, Belg. Patent 648,690, (Dec. 1964); Chem. Abstr., 63, 13504d (1965); 6, 16, 24.

125. Henkel & Cie, G.m.b.H., Brit. Patent 989,390 (Apr. 1965); Chem. Abstr., 63, 1960e (1965); 1, 12, 15, 25.

126. Henning, A. R., Kunststoffe 44, 131-3 (1954); Chem. Abstr., 48, 7925h (1954); 4, 14, 22, 24.

127. Hetflejs, J., F. Mares, and V. Chvalovsky, Intern. Symp. Organosilicon Chem., Sci. Commun., Prague, 282-9 (1965); Chem. Abstr., 66, 2122c (1967); 24, 32.

128. Hiller, C. M., O. Quast, and G. Wiedemann, Plaste Kautschuk, 11, 136-40 (1964); Chem. Abstr., 63, 10111a (1965); 5, 14, 22, 24.

129. Hinz, Wilhelm and Gerhard Solow, Silikat Tech., 8, 178-85 (1957); Chem. Abstr., 51, 17225a (1957); 4, 14, 22, 24, 32, 35.

130. Hittmair, Paul, Ernst Wohlfarth, Siegfried Nitsche, and Manfred Wick, U.S. Patent 3,432,463 (Mar. 1969); Chem. Abstr., 70, 97804w (1969); 6, 24.

131. Hoersch, F. and H. Wurtinger, Kunststoffe 56(9), 627-9 (1966); Chem. Abstr., 65, 20284e (1966); 1, 14, 22, 24, 31.

132. Holtmann, Robert, Kunststoffe 57(2), 110-16 (1967); Chem. Abstr., 67, 33191z; 1, 4, 14, 24, 31.

133. Hooker Chemical Corp., Neth. Appl. 6,400,517 (July 1964), U.S. Appl. (Jan. 1963); Chem. Abstr., 62, 4174b; 1, 21.

134. Howmet Corp., Brit. Patent 1,101,000 (Jan. 1968); Chem. Abstr., 68, 89487p (1968); 24, 33.

135. Huntsberger, J. R., Advan. Chem. Ser. 43, 180-8 (1964); Chem. Abstr., 60, 10811b (1964); 31.

136. Huntsberger, James R., J. Paint Technol., 39(507), 199-211 (1967); Chem. Abstr., 67, 3358s (1967); 32.

137. Hurley, B., Ellsworth L. Smith, Walter Kitaj, and Robert H. Kiel, Belg. Patent 612,052, (June 1962); Chem. Abstr., 57, 12122a (1962); 7, 14, 25.

138. Hutchinson, William E., U.S. Patent 3,024,131 (Mar. 1962); Chem. Abstr., 56, 14430h (1962); 7, 15, 17, 24.

139. Iannicelli, Joseph, U.S. Patent 3,290,165 (Dec. 1966); Chem. Abstr., 66, 105491b (1967); 16, 24, 33, 34.

140. Imperial Chemical Industries Ltd., Neth. Appl. 6,516,715 (Apr. 1966), Brit. Appl. (Dec. 1964, June 1965, Dec. 1965); Chem. Abstr., 65, 10751e (1966); 1, 14, 16, 24.

141. Isirikyan, A., A. V. Kiselev, and E. V. Ushakova, Kolloidn. Zh., 27(5), 690-6 (1965); Chem. Abstr., 64, 3841c (1966); 17, 24, 32.

142. Jelinek, Zdeněk K., Czech. Patent 89,064 (Mar. 1959); Chem. Abstr., 55, 23967e (1961); 14, 22.

143. Jenckel, E. and H. Huhn, Kolloid-Z., 159, 118-29 (1958); Chem. Abstr., 53, 28a (1959); 7, 12, 25

144. Joesler, Mario, Atti Congr. Intern. Materie Plastiche, 14, 228-36 (1962); Chem. Abstr., 59, 14162f (1963); 1, 4, 5, 7, 14, 16, 24, 32.

145. Johannson, O. K., F. O. Stark, G. E. Vogel, and R. M. Fleischmann, J. Compos. Mater., 1(3), 278-92 (1967); Chem. Abstr., 67, 82642f (1967); 7, 14, 24, 32.

146. Johannson, Oscar K., U.S. Patent 2,557,786 (June 1951); Chem. Abstr., 45, 8222g (1951); 7, 14, 24, 31.

147. Johnson, Albin C. and Robert C. Shaffer, U.S. Patent 3,407,169 (Oct. 1968); Chem. Abstr., 70, 20773c (1969); 1, 5, 6, 24, 34.

148. Jones, H. L., A. N. Cianciarulo, and R. L. Webb, Am. Chem. Soc., Div. Org. Coatings, Plastics Chem., Preprints 24(2), 351-9 (1964); Chem. Abstr., 64, 12877b (1966); 1, 14, 32.

149. Jones, Loren C., U.S. Patent 3,117,900 (Jan. 1964); Chem. Abstr., 60, 12235a (1964); 1, 4, 17, 24.

150. Kadowaki, Kenzo and Tsutomu Nakagiri, Japan Patent 68 13,996; Chem. Abstr., 69, 107351s (1968); 7, 16, 25.

151. Kalinina, E. I. and E. M. Lukina, U.S.S.R. Patent 173,705 (Aug. 1965); Chem. Abstr., 64, 2249g (1966); 7, 22.

152a. Kaliske, Gisbert, Dissertationen, No. 21, sheet 64.14 (1964); Chem. Abstr., 64, 2233d (1966); 5, 31.

152b. Kalnins, M., and V. Karlivane, Latv. PSR Zinat. Akad. Vestis, Kim. Ser., (3), 292-5 (1968); Chem. Abstr., 69, 78040g (1968); 7, 13, 16, 25.

153. Kanner, Bernard, U.S. Patent 3,247,280 (Apr. 1966); Chem. Abstr., 64, 19906c (1966); 1, 6, 24.

154. Kanner, Bernard, Brit. Patent 906,544 (Sept. 1962); Chem. Abstr., 58, 3575g (1963); 1, 6, 24

155. Kastrop, Clarence J., U.S. Patent 3,160,675 (Dec. 1964); Chem. Abstr., 62, 6641f (1965); 1, 5, 16, 17, 24, 31.

156. Keil, Joseph W., U.S. Patent 2,902,389 (Sept. 1959); Chem. Abstr., 54, 1920g (1960); 6, 12, 17, 24.

157. Kenyon, A. S., J. Colloid Interface Sci., 27(4), 761-71 (1968); Chem. Abstr., 69, 97398 (1968); 1, 14, 32.

158. Kisley, B. A., A. I. Mikhal'skii, V. V. Bodrova, and N. G. Korbut, Fiz.-Khim. Mekh. Orientirovannykh Stekloplast., Sb. Rab. Konf., Moscow, 30-43 (1965); Chem. Abstr., 68, 78997d (1968); 7, 14, 24, 32.

159. Koblitz, Francis F., U.S. Patent 2,774,697 (Dec. 1956); Chem. Abstr., 51, 4055g (1957); 7, 12, 14, 16, 24.

160. Kolb, Kenneth E. and John G. Koelling, Proc., Ann. Tech. Cong. SPI Reinforced Plast. Div., 21st, Chicago (1966); Chem. Abstr., 67, 12045a (1967); 1, 14, 24, 31, 32.

161. Kori, Shoichiro, Kyoka Purasuchikkusu 6, 54-60 (1960); Chem. Abstr., 57, 16153a (1962); 14, 22, 24, 32.

162. Koristek, Stanislav, Josef Hajek, and Jan Stepanek, Czech. Patent 120,411 (Nov. 1966); Chem. Abstr., 67, 102503s (1967); 4, 14, 24.

163. Korolev, A. Ya., P. V. Davydov, and L. N. Vinogradova, Vysokomolekul. Soedin., Adgeziya Polimerov, Sb. Statei, 3-11 (1963); Chem. Abstr., 60, 9331e (1964); 2, 13, 14, 24, 32.

164. Kotov, M. P. and N. S. Sorokina, Izv. Vyssh. Ucheb. Zaved., Tekhnol. Legk. Prom., (6), 66-9 (1968); Chem. Abstr., 70, 58674j (1969); 32.

165. Koval'chuk, L. M. and A. M. Chistyokov, Plast. Massy, (4), 65-6 (1968); Chem. Abstr., 69, 3529a (1968); 1, 12, 31.

166. Kramer, Max, Walter Noll, and Oda Pantke, Ger. Patent 1,080,061 (Apr. 1960); Chem. Abstr., 55, 18132d (1961); 17, 22, 24.

167. Krotova, N. A., L. P. Morozova, and B. V. Deryagin, Doklady Akad. Nauk S.S.S.R. 129, 149-52 (1959); Chem. Abstr., 54, 8220a (1960); 7, 14, 24, 32.

168. Krotova, N. A. and L. P. Morozova, Issled. v Obl. Poverkhn. Sil, Akad. Nauk SSSR, Inst. Fiz. Khim., Sb. Dokl. na Vtoroi Konf., Moscow, 322-9 (1962); Chem. Abstr., 62, 4129b (1965); 7, 14, 24, 25, 32.

169. Krotova, N. A., L. P. Morozova, A. M. Polyakov, G. A. Sokolina, and N. N. Stefanovich, Kolloidn. Zh., 26(2) 207-14 (1964); Chem. Abstr., 61, 7181h (1964); 32.

170. Krotova, N. A., L. P. Morozova, and A. M. Polyakov, Probl. Fiz.-Khim. Mekh. Voloknistykh Poristykh Dirpersnykh Strukt. Mater., Mater. Konf., Riga, 497-507 (1965); Chem. Abstr., 68, 115264k (1968); 14, 15, 32.

171. Krys'kova, B. K., A. M. Simonenko, L. N. Ol'shevskaya, and M. Z. Varentsova, Khim. Obrab. Poverkh. Steklyannogo Volokna, Vses. Nauch.-Issled. Inst. Stekloplastikov Steklyannogo Volokna, 21-6 (1966); Chem. Abstr., 68, 88088x (1968); 14, 24, 32.

172. Kryzhanovskii, B. P., A. Ya. Kuznetsov, G. V. Okatova, and M. A. Okatov, Opt.-Mekh. Prom., 35(2), 45-8 (1968); Chem. Abstr., 69, 28429v (1968); 3, 6, 14, 24.

173. Kudishina, V. A., Vestn. Mashinostr, 48(7), 44-5 (1968); Chem. Abstr., 70, 20714j (1969); 7, 13, 14, 17, 24, 25.

174. Kumins, C. A., W. M. Arnheim, and T. K. Kwei, Proc. Ann. Tech. Management Conf., Reinforced Plastics Div., Soc. Plastics Ind. 19, 11-D (1964); Chem. Abstr., 61, 16249a (1964); 14, 22, 31, 32.

175. Kuznetsova, V. P., S. I. Omel'chenko, G. N. Belogolovina, and V. G. Smelova, Sin. Fiz.-Khim. Polim., No. 5, 162-7 (1968); Chem. Abstr., 70, 5258v (1969); 2, 24.

176. Laird, J. A. and F. W. Nelson, Proc. Ann. Tech. Management Conf., Reinforced Plastics Div., Soc. Plastics Ind. 19(11-C) (1964); Chem. Abstr., 61, 16251c (1964); 1, 14, 24, 31.

177. Lawrence, Robert D. and David H. Geschwind, U.S. Patent 3,337,485 (Aug. 1967); Chem. Abstr., 68, 79066m (1968); 7, 12, 13, 17, 25.

178. Lee, Lieng-Huang, Amer. Chem. Soc., Div. Polymer Chem., Preprints 7(2), 910-15 (1966); Chem. Abstr., 66, 76732y (1967); 3, 14, 17, 32.

179. Lewis, A. F. and L. J. Forrestal, Am. Soc. Testing Mater., Spec. Tech. Publ. No. 360, 59-75 (1963); Chem. Abstr., 62, 5389b (1965); 7, 11, 12, 13, 21, 25, 32.

180. Lipatov, Yu. S., Modifkatsiya Svoistv Polimerov i Polimernykh Materialov, Akad. Nauk Ukr. SSR, Resp. Mezhvedomst Sb., 56-63 (1965); Chem. Abstr., 65, 2418h (1966); 7, 14, 16, 34.

181. Lipatov, Yu. S., Plast. Inst., Trans. J. 34(110), 83-7 (1966); Chem. Abstr., 65, 10734f (1966); 14, 16, 32, 33.

182. Lord Manufacturing Co., Brit. Patent 850,419 (Oct. 1960); Chem. Abstr., 55, 9946e (1961); 6, 12, 13, 17, 24.

183. Losev, V. B., K. B. Ryazonov, and V. D. Orlova, Plast. Massy, (2), 46 (1967); Chem. Abstr., 66, 86179n (1967) 1, 6, 17, 24.

184. Lund, Albert H., U.S. Patent 3,177,170 (Apr. 1965); Chem. Abstr., 63, 801e (1965); 1, 4, 7, 14, 24.

185. Lyutyi, V. P., N. P. Kharitonov, and L. P. Shtremt, Zh. Prikl. Khim. 38(5), 1131-3 (1965); Chem. Abstr., 63, 5829g (1965); 1, 14, 24, 34.

186. Maly, George P., U.S. Patent 3,146,142 (Aug. 1964); Chem. Abstr., 61, 12163b (1964); 1, 5, 7, 14, 17, 24, 25.

187. Manami, Hisashi and Shunichiro Nishizaki, Kogyo Kagaku Zasshi, 61, 218-19 (1958); Chem. Abstr., 54, 6171e (1960); 6, 17, 24, 34.

188. Mao, T. J., and S. L. Reegan, Proc. Symp. Adhesion Cohesion, 5th, Warren, Mich., 209-17 (1961); Chem. Abstr., 59, 14121g (1963); 7, 17, 32.

189. Markin, Yu. I., V. M. Gorchakova, V. E. Gul, and S. S. Voyutskii, Izv. Vysshikh Uchebn. Zavedenii, Khim. i Khim. Tekhnol., 5, 808-14 (1962); Chem. Abstr., 58, 12693f (1963); 7, 11, 12, 17, 32.

190. Marsden, James G., and Smauel Sterman, Fr. Patent 1,462,596 (Dec. 1966); Chem. Abstr., 67, 93658s (1967); 14, 22, 24, 33.

191. Marzocchi, Alfred, U. S. Patent 3,287,204 (Nov. 1966); Chem. Abstr., 66, 19594f (1967); 3, 14, 15, 24.

192. Marzocchi, Alfred, and Nicholas S. Janetos, U. S. Patent 3,252,825 (May 1966); Chem. Abstr., 65, 7465c (1966); 7, 14, 24.

193. Marzocchi, Alfred, and Nicholas S. Janetos, U. S. Patent 3,169,884 (Feb. 1965); Chem. Abstr., 62, 14307e (1965); 1, 14, 24.

194. Marzocchi, Alfred, and Nicholas S. Janetos, U. S. Patent 3,207,623 (Sept. 1965); Chem. Abstr., 63, 18344a (1965); 4, 14, 24.

195. Marzocchi, Alfred, and Nicholas S. Janetos, Ger. Patent 1,141,788 (Dec. 1962); Chem. Abstr., 58, 14225f (1963); 1, 14, 24, 25.

196. Marzocchi, Alfred, and Nicholas S. Janetos, U. S. Patent 2,931,739 (Apr. 1960); Chem. Abstr., 54, 16921g (1960); 1, 4, 14, 24.

197. Masters, John E., U. S. Patent 3,150,116 (Sept. 1964); Chem. Abstr., 61, 16264g (1964); 1, 24.

198. Matonis, V. A., Polym. Eng. & Sci., 9(2), 100 (1969); 24, 32.

199. Matting, Alexander, and W. Brockmann, Adhaesion, (8), 343-51 (1968); Chem. Abstr., 70, 78619y (1969); 5, 32, 33.

200. McWhorter, Wayne F., U. S. Patent 3,154,597 (Oct. 1964); Chem. Abstr., 62, 1811a (1965); 1, 14, 24.

201. Meitin, Yu. V., Plasticheskie Massy, (12), 48-53 (1964); Chem. Abstr., 62, 6610d (1965); 14, 22, 24, 32.

202. Michelin, Durin & Cie, Fr. Patent 1,278,030 (Mar. 1962); Chem. Abstr., 57, 4890h (1962); 1, 16, 17, 25.

203. Midland Silicones Ltd., Brit. Patent 813,889 (May 1959); Chem. Abstr., 53, 19464f (1959); 6, 14, 24.

204. Minnesota Mining and Manufg. Co., Belg. Patent 654,206 (Feb. 1965); Chem. Abstr., 64, 14418f (1966); 1, 14, 24.

205. Moebes, W., and A. Wende, Plaste Kautschuk, 9, 232-6 (1962); Chem. Abstr., 63, 4468c (1965); 6, 14, 24, 32.

206. Monsanto Co., Neth Appl. 6,415,099 (June 1965); Chem. Abstr., 64, 892a (1966); 4, 7, 17, 21, 34.

207. Monsanto Co., Neth. Appl. 6,413,905 (Dec. 1965); Chem. Abstr., 64, 16016a (1966) 24, 34.

208. Monsanto Co., Neth. Appl. 6,600,164 (July 1966); Chem. Abstr., 66, 19216j (1967); 24, 34.

209. Morgan, Albert W., and Jack S. Swenson, U. S. Patent 3,376,278 (April 1968); Chem. Abstr., 68, 105746e (1968); 7, 16, 25, 33.

210. Morgan, Willard L., U. S. Patent 3,013,915 (Dec. 1961); Chem. Abstr., 56, 11807a (1962); 14, 16, 24.

211. Morozova, L. P., and N. A. Krotova, Issled. Obl. Poverkh. Sil, Sb. Dokl. Konf., 3rd., 442-7 (1966); Chem. Abstr., 70, 4852 (1969); 14, 24, 32.

212. Muchnick, Samuel N., Mech. Eng., 78, 19-22 (1956); Chem. Abstr., 50, 2389f (1956); 12, 17, 32, 33.

213. Mueller, Ulrich, & Gottfried Wiedemann, Faserforsch. Textiltech., 20(1), 10-20 (1969); Chem. Abstr., 70, 97855p (1969); 14, 22, 24, 32.

214. Nack, Herman R., U. S. Patent 2,791,515 (May 1957); Chem. Abstr., 51, 12460c (1957); 17, 22.

215. Nakabayashi, Tadaaki, Atsushi Ikari, and Jiro Tsukamoto, Chem. High Polymers, 11, 123-6 (1954); Chem. Abstr., 50, 1362g (1956); 5, 25.

216. Nebesar, Robert J., U. S. Patent 2,607,708, (Aug. 1952); Chem. Abstr., 46, 11616d (1952); 6, 14, 22.

217. Nielson, Lawrence E., J. Appl. Polymer Sci., 10(1), 97-103 (1966); Chem. Abstr., 64, 11381d (1966); 32, 34.

218. Nitrogenmuvek, Peti, Utugyi Kutato Intezet, and Novenyolajes Haztartasi Vegyipari Kutato Intezet, Hung. Patent 151,460, (June 1964); Chem. Abstr., 61, 7198c (1964); 7.

219. Nitzsche, S., Kunststoffe, 41, 87-8 (1951); Chem. Abstr., 45, 5968b (1951); 14, 24.

220. Nitzsche, S., Manfred Wick, and Ernst Wohlfahrth, Ger. Patent 1,205,279, (Nov. 1965); Chem. Abstr., 64, 5276g (1966); 6, 14, 17, 24.

234c. Pines, Arthur N., and Samuel Sterman, Brit. Patent 952,992, (Mar. 1964); *Chem. Abstr.*, *61*, 16312h (1964); 1, 6, 17, 24.

235. Plueddemann, E. P., *J. Paint Technol.*, *40*(516), 1-9 (1968); *Chem. Abstr.*, *68*, 60553w (1968); 14, 17, 24, 29, 32.

236. Plueddemann, E. P., *Proc. Ann. Tech. Conf. SPI Reinforced Plastics Div., 20th, Chicago 1965*, 19-A; *Chem. Abstr.*, *63*, 3124c (1965); 7, 14, 16, 24, 29.

237. Plueddemann, E. P., *Proc. Ann. Tech. Conf. SPI Reinforced Plastics Div., 21st, Chicago 1966* (Sect. 3D); *Chem. Abstr.*, *65*, 10732a (1966); 7, 14, 24, 31.

238. Plueddemann, E. P., *Proc. Ann. Tech. Conf., SPI Reinf. Plast. Div. 1967*, 9-A; *Chem. Abstr.*, *67*, 54674z (1967); 14, 16, 24 31, 32.

239. Plueddemann, E. P., Fr. Patent 1,460,691, (Dec. 1966); *Chem. Abstr.*, *67*, 22542p (1967); 1, 5, 7, 14, 16, 24.

240. Plueddemann, E. P., Fr. Patent 1,492,467 (Aug. 1967); *Chem. Abstr.*, *68*, 105796w (1968); 7, 14, 17, 24, 31.

241. Plueddemann, E. P., H. A. Clark, L. E. Nelson, and K. R. Hoffman, *Modern Plastics*, 135 (Aug. 1965); 1, 4, 14, 24, 31.

242. Pohl, G., *Plaste Kaut.*, *15*(8), 565-8 (1968); *Chem. Abstr.*, *69*, 52697b (1968); 4, 14, 24, 32.

243. Polmanteer, Keith E., U. S. Patent 3,155,633, (Nov. 1964); *Chem. Abstr.*, *62*, 4178h (1965); 6, 13, 15, 24, 34.

244. Polniaszek, M. C., R. H. Schaufelberger, *Adhes. Age*, *11*(7), 25-7 (1968); *Chem. Abstr.*, *69*, 52694y (1968); 1, 5, 6, 7, 12, 24.

245. Powell, Robert E., Brit. Patent 1,132,573, (Nov. 1968); *Chem. Abstr.*, *70*, 20871h (1969); 4, 17, 25, 35.

246. Prutkov, L. M., K. A. Andrianov, N. A. Polikanin, and E. Z. Asnovich, U. S. S. R. Patent 171,577, (May 1965); *Chem. Abstr.*, *63*, 15067g (1965);1, 6, 24.

247. Riley, Ivor H., Hewart W. Winnam, Brit. Patent 1,014,272, (Dec. 1965); *Chem. Abstr.*, *64*, 8455b (1966); 6, 17, 24.

248. Rittenhouse, Robert C., Ger. Patent 1,107,860 (May 1960); Chem. Abstr., 56, 2550f (1962); 1, 15, 17, 24.

249. Rittenhouse, Robert C., Brit. Patent 952,993, (Mar. 1964); Chem. Abstr., 61, 5888d (1964); 6, 12, 15, 16, 17, 24.

250. Rogers, Narvel L., Appl. Poly. Symp. 3(1-25), 327-40 (1966); Chem. Abstr., 66, 88091b (1967); 11, 12, 13, 17.

251. Roseland, R. M., Proc., Ann. Tech. Conf., SPI Reinforced Plastics Div., 21st, Chicago 1966 (Sect. 4C); Chem. Abstr., 65, 11789e (1966); 24, 31.

252. Ruetgerswerke and Teerverwertung A.-G., Neth. Appl. Patent 6,510,320, (Feb. 1966); Chem. Abstr., 65, 15621e (1966); 1, 22, 24, 34.

253. St. Cyr, Marjorie C., William C. Tanner, U. S. Dept. Com., Office Tech. Serv., AD275,432, (1962); Chem. Abstr., 59, 10301h (1963); 6, 17, 31.

254. Saint-Gobain, Compagnie de, Fr. 1,473,183, (Mar. 1967); Chem. Abstr., 67, 76007m (1967); 4, 7, 14, 24, 25.

255. Santt, Rene C., Fr. Patent 1,468,848, (Feb. 1967); Chem. Abstr., 68, 70281v (1968); 12, 16, 25.

256. Sanzharovskii, M. S., Dyl'kov, and P. I. Zubov, Lakokrasochnye Materialy i ikh Primenenie 1964(6), 17-21; Chem. Abstr., 62, 8000c (1965); 7, 13, 31, 32.

257. Sato, Hideshi, John E. Rutzler, Jr., Am. Chem. Soc., Div. Paint, Plastics, Printing Ink Chem., Preprints 20, No. 1, 124-35 (1960); Chem. Abstr., 57, 4874f (1962); 1, 5, 32.

258. Sayre, Kenneth L., U. S. Patent 2,785,085, (Mar. 1957); Chem. Abstr., 51, 7059h (1957); 1, 14, 16, 24.

259. Scala, Luciano C., Daniel W. Lewis, Ger. Patent 1,263,887, (Mar. 1968); Chem. Abstr., 68, 96538j (1968); 6, 7, 17, 24.

260. Schiller, Arthur M., George A. Tanner, and Armand F. Lewis, U. S. Patent 3,309,261, (Mar. 1967); Chem. Abstr., 66, 105648h (1967); 2, 12, 13, 24.

261. Schonhorn, H., and L. H. Sharpe, J. Polymer Sci., Pt. A, 3(9) 3087-97 (1965); Chem. Abstr., 63, 15049d (1965); 1, 12, 16, 32, 33.

262. Schonhorn, Harold, J. Polymer Sci., Pt. A, 1, 2343-59 (1963); Chem. Abstr., 59, 6579h (1963); 7,12, 17, 25, 33, 35.

263. Schrader, Malcolm E., and Irving Lerner, U. S. Patent 3,404,023, (Oct. 1968); Chem. Abstr., 70, 5027u (1969); 1, 14, 16, 21.

264. Schrader, Malcolm, Irving Lerner, and Leo Deutsch, AD638753 (1966); Chem. Abstr., 67, 14474c (1967); 14, 21, 32.

265. Schrader, Malcolm E., and Irving Lerner, Nature 204(4960), 759-61 (1964); Chem. Abstr., 62, 5925b (1965); 14, 21, 32.

266. Schrader, Malcolm E., and Irving Lerner, Proc., Anniv. Tech. Conf. SPI Reinforced Plastics Div., 20th, Chicago 1965, (3-C); Chem. Abstr., 63, 11794e (1965); 1, 14, 21, 32.

267. Schrader, M. E., I. Lerner, F. J. D'Oria, Mod. Plast., 45(1) 195-7, 268, 272, 276, 280, 282 (1967); Chem. Abstr., 69, 11047w (1968); 1, 14, 24, 31, 32.

268. Schrader, M. E., I. Lerner, F. J. D'Oria, and L. Deutsch, Proc., Ann. Tech. Conf., SPI Reinf. Plastics Div., 22nd, Washington, D. C. 1967, 13-A; Chem. Abstr., 67, 74254r (1967); 1, 14, 21, 24, 31, 32.

269. Schultz, Harold, and Clarence G. Zike, Ger. Patent 1,091,748, (Oct. 1960); Chem. Abstr., 55, 25364g (1961); 1, 24.

270. Schwaner, K., Plaste u. Kautschuk 7, 59 (1960); Chem. Abstr., 54, 16007f (1960); 2, 12, 24, 31.

271. Selin, Terry G., U. S. Patent 3,277,047, (oct. 1966); Chem. Abstr., 66, 29853d (1967); 6, 13, 14, 15, 16, 17, 24.

272. Sergovic, John A., U. S. Patent 3,328,231, (June 1967); Chem. Abstr., 67, 74178u (1967); 17, 24, 33.

273. Shafrin, Elaine G., and William A. Zisman, Advan. Chem. Ser. 1968, No. 87, 20-37; Chem. Abstr., 70, 39109n (1969); 7, 17, 25.

274. Sheratte, Martin B., and John A. Scott, U. S. Patent 3,231,425, (Jan. 1966); Chem. Abstr., 64, 12324h (1966); 1, 11, 12, 13, 17, 25, 33.

275. Shiryaeva, G. V., G. D. Andreevskaya, and L. V. Belunova, Vysokomolekul. Soedin., Adgeziya Polimerov, Sb. Statei 1963 103-6 (1963); Chem. Abstr., 60, 10872h (1964); 4, 14, 22, 24.

276. Simpson, Verne G., Fr. Patent 1,419,909, (Dec. 1965); *Chem. Abstr.*, *65*, 10761f (1966); 15, 17, 24.

277. Smith, Theodore R., and Arthur N. Pines, U. S. Patent 3,248,358, (April 1966); *Chem. Abstr.*, *65*, 921b (1966); 12, 13, 24.

278. Smith-Johannsen, Robert, U. S. Patent 2,643,964, (June 1953); *Chem. Abstr.*, *48*, 397b (1954); 6, 13, 14, 24.

279. Snogren, Richard C., IAA Accession No. A6638489 (1966); *Chem. Abstr.*, *67*, 5295t (1967); 12, 17, 33.

280. Societe du Verre Textile, Fr. Patent 1,519,659, (Apr. 1968); *Chem. Abstr.*, *70*, 97734y (1969); 1, 14, 24, 25.

281. Societe des Usines Chimiques Rhone-Poulenc, Belg. Patent 611,687, (June 1962); *Chem. Abstr.*, *57*, 12688b (1962); 2, 24.

282. Solomko, V. P., V. V. Poletukha, I. A. Uskov, and A. G. Zhigotskii, *Ukr. Khim. Zh.*, *30*(3), 305-8 (1964); *Chem. Abstr.*, *61*, 2005g (1964); 7, 14, 16, 24, 32, 34.

283. Speier, John L., Jr., Ger. Patent 1,090,399, (Oct. 1960); *Chem. Abstr.*, *55*, 27997e (1961); 7, 14, 24.

284. Stastny, Fritz, Rudolf Breu, Heinz H. Koerner, Fr. Patent 1,507,897, (Dec. 1967); *Chem. Abstr.*, *70*, 12730w (1969); 1, 14, 17, 24.

285. Stauffer Chemical Co., Neth. Patent Appl. 6,612,420, (Mar. 1967); *Chem. Abstr.*, *67*, 44951y (1967); 14, 17, 24, 31.

286. Stegemann, Walter, and Göttfried Gunther, Ger. Patent 952,921, (Nov. 1956); *Chem. Abstr.*, *53*, 14570i (1959); 2, 15, 16, 17, 24.

287. Stein, George A., and Elwood R. Pelton, U. S. Patent 3,246,671, (Apr. 1966); *Chem. Abstr.*, *65*, 9123g (1966); 1, 2, 17, 24, 31.

288. Steinman, Robert, U. S. Patent 2,611,718, (Sept. 1952); *Chem. Abstr.*, *47*, 844d (1953); 7, 14, 22.

289. Steinman, Robert, U. S. Patent 2,688,006, (Aug. 1954); *Chem. Abstr.*, *49*, 4253b (1955); 7, 14, 24, 33.

290. Sterman, S., and J. G. Marsden, *Mod. Plastics*, *40*(11), 125, 127, 129-30, 134, 136, 138, 177 (1963); *Chem. Abstr.*, *59*, 10299d (1963); 7, 14, 24, 34.

291. Sterman, S., and J. G. Marsden, Mod. Plastics, 41(2), 254, 261-2, (1963); Chem. Abstr., 60, 721h (1964); 14, 17, 24, 32, 34.

292. Sterman, S., and J. G. Marsden, Plastics Technol. 9(5), 38-41 (1963); Chem. Abstr., 59, 4113f (1963); 1, 4, 5, 7, 24, 34.

293. Sterman, S., and J. G. Marsden, Polymer Eng. Sci. 6(2), 97-112 (1966); Chem. Abstr., 64, 17794d (1966); 7, 24, 34.

294. Sterman, S., and J. G. Marsden, SPE Tech. Papers 1963, 67-82; Chem. Abstr., 60, 1883e (1964); 1, 4, 5, 7, 14, 16, 24.

295. Sterman, S., and J. G. Marsden, Proc., Ann, Tech. Conf., SPI Reinf. Plastics Div., 21st, Chicago 1966 (Sect. 3A); Chem. Abstr., 66, 19315r (1967); 7, 14, 24.

296. Sterman, S., and J. G. Marsden, U. S. Patent 3,259,518, (July 1966); Chem. Abstr., 65, 15619e (1966); 1, 7, 14, 24.

297. Sukhareva, L. A., Yu. P. Smirnova, P. I. Zubov, A. V. otova, and R. Ya. Khvilivitskii, Plasticheskie Massy 1965(10), 31-4; Chem. Abstr., 64, 869c (1966); 1, 4, 14, 24.

298. Takada, Shigeyuki, and Yuzo Muira, Japan. Patent 5030 (Oct. 1953); Chem. Abstr., 48, 11113i (1954); 5, 14, 17, 24, 34.

299. Taylor, Dean, Jr., and John E. Rutzler, Jr., Ind. Eng. Chem., 50, 928-34 (1958); Chem. Abstr., 52, 16005t (1955); 7, 13, 16, 17, 32.

300. Te Grotenhuis, Theodore A., U. S. Patent 3,249,461, (May 1966); Chem. Abstr., 65, 2438b (1966); 1, 4, 5, 14, 24.

301. Ter-Minassian-Saraga, Lisbeth, Compt. Rend., 260(22) (Groupe 7), 5770-3 (1965); Chem. Abstr., 63, 4979h (1965); 32.

302. Tertykh, E. A., A. A. Chuiko, and I. E. Neimark, Kolloidn. Zh. 28(2), 278-82 (1966); Chem. Abstr., 65, 4042a (1966); 24, 32, 34.

303. Thinius, K., and G. Grosse, Plaste u. Kautschuk, 5, 418-21 (1958); Chem. Abstr., 53, 9717d (1959); 32.

304a. Thompson, L. M., and W. E. Hill, "A Preliminary Evaluation of Silane Coupling Agents as Primers and Additives in Polyurethane Bonding Procedures," NASA TM X-53676; 2, 12, 24, 31.

304b. Ibid., unpublished data.

305. Tiede, Ralph L., U. S. Patent 3,253,948 (May 1966); *Chem. Abstr.*, *65*, 5193d (1966); 5, 14, 24, 31.

306. Tolstaya, S. N., S. S. Mikhailova, V. M. Luk'yanovich, and E. I. Evko, *Kolloid. Zh. 29*(6), 892-3 (1967); *Chem. Abstr.*, *68*, 30558v (1968); 7, 32, 34.

307. Trebilcock, John W., U. S. Patent 3,185,717 (May 1965); *Chem. Abstr.*, *63*, 9515c (1965); 16, 22.

308. Trivisonno, Nicholas M., Lieng-Huang Lee, and Selby M. Skinner, *Ind. Eng. Chem.*, *50*, 912-17 (1958); *Chem. Abstr.*, *52*, 15951b (1958); 14, 32, 33.

309. Trostyanskava, E. B., A. M. Poimanov, and Yu. N. Kazanskii, *Mekhan. Polimerov*, *Akad. Nauk Latv. SSR*, (1), 26-35 (1965); *Chem. Abstr.*, *63*, 1939f (1965); 1, 5, 6, 7, 14, 24, 25.

310. Trostyanskava, E. B., A. M. Poimanov, and Yu. N. Kazanskii, *Plasticheskie Massy*, (8), 20-3 (1964); *Chem. Abstr.*, *61*, 12144g (1964).

311. Trostyanskaya, E. B., and G. M. Gunyaev, *Plast. Massy*, (5), 30-4 (1967); *Chem. Abstr.*, *67*, 54713m (1967); 1, 5, 14, 24.

312. Tutas, D. J., R. Stromberg, and E. Passaglia, *SPE Trans.*, *4*(4), 256-62 (1964); *Chem. Abstr.*, *62*, 4216a (1965); 14, 24, 32.

313. Tyler, Leslie J., U. S. Patent 3,170,962 (Feb. 1965); *Chem. Abstr.*, *62*, 13388h (1965); 1, 6, 17, 24.

314. Uklonskii, D. A., E. S. Borodavchenko, V. V. Severnyi, and V. N. Slepich, U.S.S.R. Patent 193,066, *Chem. Abstr.*, *68*, 79061f (1968); 6, 24, 31.

315. Unilever, N. V., Fr. Patent 1,364,168 (June 1964); *Chem. Abstr.*, *61*, 14901d (1964); 6, 14, 24.

316. Uniroyal, Inc., Neth. Appl. 6,610,535 (Feb. 1967); *Chem. Abstr.*, *67*, 100856k (1967); 3, 15, 16, 25.

317. Vanderbilt, Byron M., and Robert E. Clayton, U. S. Patent 3,307,967 (Mar. 1967); *Chem. Abstr.* *66*, 86471b (1967); 3, 14, 15, 24.

318. Vanderbilt, Byron M., U. S. Patent 3,301,739 (Jan. 1967); *Chem. Abstr.*, *66*, 95896w (1967); 7, 14, 24.

319. Vanderbilt, Byron M., and Robert E. Clayton, Ind. Eng. Chem., Prod. Res. Develop., 4(1), 18-22 (1965); Chem. Abstr., 62, 9330c (1965); 7, 14, 15, 24.

320. Vanderbilt, Byron M., and John J. Jurazelski, Ind. Eng. Chem., Prod. Res. Develop., 1, 188-94 (1962); Chem. Abstr., 57, 12711f (1962); 7, 14, 24, 34.

321. Vereinigung Volkseigener Betriebe Haushalt- und Verpackungsglas Weisswasser, Fr. Patent 1,411,565 (Sept. 1965); Chem. Abstr., 65, 4061a (1966); 1, 14, 17, 24, 31.

322. Vereinigung Volkseigener Betriebe Haushalt- und Verpackungsglas Weisswasser, Belg. Patent 653,776 (Mar. 1965); Chem. Abstr., 65, 7402g (1966); 1, 14, 17, 24, 31.

323. Viventi, R. V., H. T. Plant and R. T. Maker, Modern Plastics, 268 (Nov. 1968); 7, 14, 16, 24.

324a. Vinogradova, L. M., and A. Ya. Korolev, Vysokomol. Soedin., Ser. B, 11(2), 126-9 (1969); Chem.Abstr., 70, 107562g (1969); 7, 12, 13, 25, 32.

324b. Vlasova, K. N., and L. A. Rodivilova, Plasticheskie Massy, No. 2, 19-23 (1960); Chem. Abstr., 54, 23421i (1960); 7, 12, 13, 15, 17, 31.

325. Vogel, G. E., O. K. Johannson, F. O. Stark, and R. M. Fleischmann, Proc. Annu. Tech. Conf., SPI, Reinf. Plast. Div., 13-B, (1967); Chem. Abstr., 67, 33230m (1967); 1, 7, 14, 24, 34.

326. Voronkov, M. G., E. A. Lasskaya, and A. A. Pashchenko, Zh. Prikl. Khim., 38(7), 1483-7 (1965); Chem. Abstr. 63, 11868c (1965); 14, 24, 32.

327. Voyutskii, S. S., V. G. Raevskii, and S. M. Yagnyatinskaya, Zh. Vses. Khim. Obshchestva im. D. I. Mendeleeva, 9(1), 114-15 (1964); Chem. Abstr., 61, 807h (1964); 3, 14, 15, 24.

328. Voyutskii, S. S., and Yu. I. Markin., Vysokomolekul. Soedin., 4, 926-34 (1962). Chem. Abstr., 59, 1817d (1963); 3, 12, 17, 35.

329. Wacker-Chemie G.m.b.H., Fr. Patent 1,361,847 (May 1964); Chem. Abstr., 62, 5425d (1965); 3, 14, 15, 24.

330. Waterhouse, R. B., and J. H. Schulman, J. Oil & Colour Chemists' Assoc., 38, 646-51 (1955); Chem. Abstr., 50, 16267 (1956); 11, 12, 13, 25, 32.

331. Wegman, Raymond F., Adhes. Age, 10(1), 20-7 (1967); Chem. Abstr., 66, 116318b (1967); 1, 12, 22, 32.

332. Weisbart, Hans, Kunststoffe, 54(12), 784-90 (1964); Chem. Abstr., 62, 7474h (1965); 1, 4, 7, 14, 24, 31, 34.

333. Weisbart, Hans, Proc., Anniv. Tech. Conf., SPI, Reinforced Plastics Div., 20th., Chicago, 3-D, (1965); Chem. Abstr., 63, 3989e (1965); 7, 14, 25.

334. Weisbart, Hans, Edith Behnke, and Gunther Eckolt, Ger. Patent, 1,022,380 (Jan. 1958); Chem. Abstr., 54, 11425d (1960); 4, 14, 22.

335. Weiss, P., Dechema Monograph, 51(885-894), 99-113 (1964); Chem. Abstr., 62, 13322f (1965); 1, 16, 32.

336. White, Thomas E., Proc., Anniv. Tech. Conf. SPI, Rein. Plastics Div., 20th, Chicago, 3-B (1965); Chem. Abstr., 63, 7675c (1965); 14, 24, 32.

337. Wiedemann, Gottfried, Ursulla Renner, and Brigitte Ziegenspeck, Faserforsch. Textiltech., 17, 444-52 (1966); Chem. Abstr., 66, 38793m (1967); 6, 14, 22, 24, 32.

338. Wismer, Marco, Vernon G. Ammons, and Gerald W. Miller, Fr. Patent 1,475,917 (Apr. 1967); Chem. Abstr., 67, 91439x (1967); 2, 6, 14, 24.

339. Wissinger, Samuel E., Jr., U. S. Patent 3,291,633 (Dec. 1966); Chem. Abstr., 66, 48931u (1967); 14, 22.

340. Yaeger, Luther L., U. S. Patent 3,193,429 (July 1965); Chem. Abstr., 63, 11144c (1965); 7, 14, 24.

341. Yaeger, Luther L., Ger. Patent 1,034,075 (July 1958); Chem. Abstr., 54, 26023a (1960); 5, 6, 7, 14, 24, 34.

342. Yao, Yung-Fang Yu, J. Phys. Chem., 68(1), 101-5 (1964); Chem. Abstr., 60, 4831h (1964); 13, 23, 32.

343. Yates, Paul C., and Trebilcock, Reinforced Plastics Div. Soc. of Plastics Ind., 16, 8-B (1961); 4, 14, 22, 32.

344. Young, Freeman M., and L. L. Rouch, Amer. Chem. Soc., Div. Org. Coatings Plast. Chem., Preprints, 27(2), 110-18 (1967); Chem. Abstr., 70, 99910b (1969); 13, 14, 25, 32.

345. Zhinkina, L. N., L. N. Severnyi, and T. F. Altukhova, Kremniiorg. Soedin., Tr. Soveshch, No. 3, 77-81 (1967); Chem. Abstr., 69, 107312e (1968); 7, 24.

346. Zisman, W. A., I&EC Product Research and Development, 8(2), 98-110 (1969); 14, 22, 24, 32.

B. BIBLIOGRAPHY OF BOOKS AND REVIEWS

1. Alner, David J. "Aspects of Adhesion" Vol. 1-4. Univ. of London Press, London, Annual Review.
2. Alter, Harvey, University Micorfilms; Ann Arbor, Michigan. Order No. 61-6692, 68 pp. Dissertation Abstr. 22, 3002, 1962.
3. Anderson, C. Clement. Ind. Eng. Chem. 60(8), 80-7, 1968.
4. Anon. Adhesive Age 3. No. 9, 30-4, 1960.
5. Baier, R. E., Shafrin, Elaine G., Zisman, William A. Science. 162(3860), 1360-8, 1968.
6. Baumann, Hans. Leime und Kontaktkleber; Theoretische Grundlagen, Eigenschaften, Anwendung. Springer-Verlag, Berlin, 1967.
7. Beach, Norman E. Plast. Tech. Eval. Center. Note No. 14, 90 pp., 1966.
8. Bikerman, J. J. "The Science of Adhesive Joints" 2nd Ed. Academic, New York, 1968.
9. Bikerman, Jacob J. Ind. Eng. Chem. 59(9), 40-4, 1967.
10. Bikerman, J. J. Am. Chem. Soc., Div. Polymer Chem. Preprints 5(2), 566-7, 1964.
11. Bikerman, J. J. Encycl. Polymer Sci. Technol. 1, 477-82, 1964.
12. Clark, F., Rutzler, J. E., Jr., and Savage, R. L. London: Soc. Chem. Ind., 229 pp., 1954.
13. De Bruyne, N. A. Plastics (London). 16, 308-9, 1951.
14. Fiske, R. L. Adhesives Age. 4(10), 33-7, 1961.
15. Frissel, W. J. Encycl. Polym. Sci. Technol. 6, 740-63, 1967.
16. Fukumura, Masuo. Nippon Secchaku Kyokai Shi. 3(2), 90-8, 1967.
17. Genzsch, Erwin O. Gas-Wasserfach. 103, 997-1000, 1962.
18. Gorbatkina, Yu. Adhaesion. 10(5), 201-6, 208, 210, 1966.

BIBLIOGRAPHY OF BOOKS AND REVIEWS (CONT'D.)

19. Gray, V. R. Chem. Ind. (London). 23, 969-78, 1965.

20. Hata, Toshio. Shikizai Kyokaishi. 39(12), 599-609, 1966.

21. Hauserman, F. B. Advances in Chem. Ser. 23, 338-56, 1959.

22. Houwink, R. Kolloid-Z. 151, 143-7, 1957.

23. Houwink, Roelof and Salomon, G. "Adhesion and Adhesives," Vol. 1: Adhesives, 2nd Ed. Elsevier, New York, 1965.

24. Huang, Ching Yun. Kagaku No Ryoiki. 20(9), 685-95, 1966.

25. Imoto, Tatsuya. Nippon Gomu Kyokaishi. 39(10), 761-99, 1966.

26. Jaeger, F. Kautschuk Gummi Kunststoffe. 18(3), 155-62, 1965.

27. Joesler, Mario. Materie Plastiche Elastomeri. 29(5), 652-60, 1963.

28. Jurecic, Anton. Tappi. 49(7), 306-10, 1966.

29. Kanamaru, Kisou. Kobunshi. 17(197), 740-9, 1968.

30. Kardashov, D. A. Tr. Vses. Konf. Kleyam Tekhnol. Skleivaniya, 1st. 5-26, 1966.

31. Keith, R. E., Randall, M. D., and Martin, D. C. Spec. Publ. NASA-SP-5085, 1967. Avail. Dep., CFSTI. Nucl. Sci. Abstr. 22(10), 19517, 1968.

32. Kline, G. M. and Reinhart, F. W. Mech. Eng. 72, 717-22, 1950.

33. Kotov, M. P. Izv. Vysshikh Uchebn. Zavedenii, Tekhnol. Legkoi Prom. 6, 29-36, 1964.

34. Kumaran, P. S. Sampath. Univ. Microfilms, Ann Arbor, Michigan. L.C. Card No. Mic 60-6447, 71 pp. Dissertation Abstr. 21, 2507, 1961.

BIBLIOGRAPHY OF BOOKS AND REVIEWS (CONT'D.)

35. Levine, Harold H. *Ind. Eng. Chem. 54*. *No. 3*, 22-5, 1962.

36. Maheo, James J. *Adhesives Age 3*. *No. 4*, 35-7, 1960.

37. Mark, H. F. *Dechema Monograph*. *51(885-894)*, 59-96, 1964.

38. Marsden, J. G. and Sterman, S. *Amer. Chem. Soc. Org. Coatings Plastics Chem. Preprints 25(2)*, 91-100, 1965.

39. Matting, A. and Brockmann, W. *Angew. Chem., Int. Ed. Engl. 7(8)*, 598-605, 1968.

40. Michel. *Adhaesion*. 10(4), 153-7, 1966.

41. Mittrop, F. *Tech. Mitt. 57(8)*, 387-93, 1964.

42. Moskvitin, N. I. *Physiocochemical Principles of Gluing and Adhesion Processes*. SFCSI-Agr (TT-68-50368), 1969.

43. Mueller, R. *Tech. Mitt*. 57(7), 303-9, 1964.

44. Nakao, Kazumune. *Nippon Secchaku Kyokai Shi*. *3(4)*, 233-44, 1967.

45. Nakazawa, Shoji, Kadowaki, Kenzo, and Nakagami, Teruo. *Senryo To Yakuhin*. *12(5)*, 186-95, 1967.

46. Newhall, R. G. "Metal-to-Metal Adhesives for the Assembly of Aircraft." Western Business Pubs., San Francisco, 1955.

47. Okawara, M. *Nippon Secchaku Kyokai Shi*. *4(1)*, 9-19, 1968.

48. Parker, R. S. R. and Taylor, P. *Adhesion and Adhesives*. Pergamon, New York, 1966.

49. Plueddemann, E. P. *Reinforced Plastics Div., 20th, Chicago*. *19-A*, 10 pp., 1965.

50. Plueddemann, E. P. *J. Paint Technol*. *40(516)*, 1-9, 1968.

51. Reichel, Sigrid. *Plaste Kaut*. 15(7), 501-4, 1968.

52. Rutzler, John E., Jr. *Adhesives Age 2*. *No. 6*, 39-43, 1959 and No. *7*, 28-31.

BIBLIOGRAPHY OF BOOKS AND REVIEWS (CONT'D.)

53. Schnurrbusch, K. Plaste u. Kautschuk 4. 45-7, 53, 1957.

54. Seidler, P. O. Adhaesion. 7(11), 503-8, 510-12, 1963.

55. Simmler, W. Mitt. Ver. Deut. Emailfachleute. 13(11), 77-80, 1965.

56. Stadelmann, L. Gummi u. Asbest 13. 356, 358, 360, 432, 434, 436, 444, 1960.

57. Sterman, Samuel and Marsden, James G. Ind. Eng. Chem. 58(3), 33-7, 1966.

58. Sterman, S. and Marsden, J. G. Mod. Plast. 44-6, 169-73, 1967.

59. Sterman, S. and Marsden, J. G. Fundam. Aspects Fiber Reinf. Plast. Compos., Conf., Dayton, Ohio. 245-73, 1966.

60. Thelen, Edmund. J. Appl. Polymer Sci. 6, 150-4, 1962.

61. Vasenin, R. M. Adhesives Age. 8(5), 18-25, 6, 30-5, 1965.

62. Voyutskii, S. S. and Vakula, V. L. J. Appl. Polymer Sci. 7, 475-91, 1963.

63. Voyutskii, S. S. and Vakula, V. L. Uspekhi Khim. 28, 701-40, 1959.

64. Wake, W. C. Roy. Inst. Chem. (London) Lect. Ser. 4, 31 pp., 1966.

65. Walter, Alexander H. Deut. Farben-Z. 22(7), 281-6, 1968.

66. Weiss, Philip. J. Polymer Sci. Pt C No. 12, 169-83, 1966.

67. Weiss, Philip. New York: Elsevier Pub. Co., 272 pp., 1962.

68. Zisman, W. A. Encycl. Polymer Sci. Technol. 1, 445-77, 1964.