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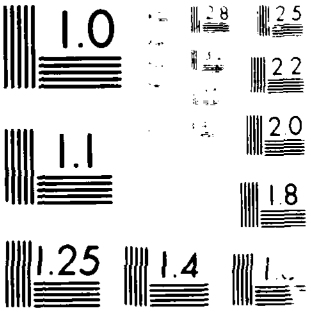
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WATER DISBONDMENT CHARACTERIZATION OF ORGANIC COATING/METAL SUBSTRATE SYSTEMS

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19. ABSTRACT *(Continue on reverse if necessary and identify by block number)*

The adhesion of many organic coatings to metal substrates is adversely affected by exposure to an aqueous environment. Even high relative humidities can cause coating disbondment to occur. The mechanism behind this adhesion loss is the accumulation of water molecules at small preexisting unbonded areas at the coating/substrate interface. Water diffuses through the coating under a concentration gradient, condenses in these areas and causes them to grow. As these areas grow laterally, they cause stresses to occur at the coating/substrate interface which eventually leads to the adhesion loss. The more primary chemical adhesive bonds a specific coating makes with the substrate the more resistant that system is to water disbondment. (over)

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19. ABSTRACT (continued)

To study this loss of adhesion caused by water, a number of coating/substrate combinations were evaluated. The coatings were selected to cover a wide range of adhesion qualities (i.e. differing numbers of primary and secondary chemical adhesion bonds). The substrates were selected to provide a variety of different surface oxides. First, the water disbondment nature of the coating/substrate systems was determined using a water immersion adhesion test. This test consisted of removing coated metal coupons from the test solutions periodically, drying the coating surface and then measuring the adhesion of the coating to the substrate using a tape pull-off test. The exposure time, amount of coating removal and any other observations were recorded. Second, an internal reflectance FTIR analysis technique was used to characterize the coating/substrate and coating/air interfaces for some of these systems. Test specimens for this FTIR technique consisted of vapor-deposited, thin metal films coated with the neat polymer. The results from this investigation showed that systems exhibiting primary chemical interactions at the interface had a greater resistance to wet adhesion loss than materials with only secondary interactions. This result correlates well with the water disbondment theory.

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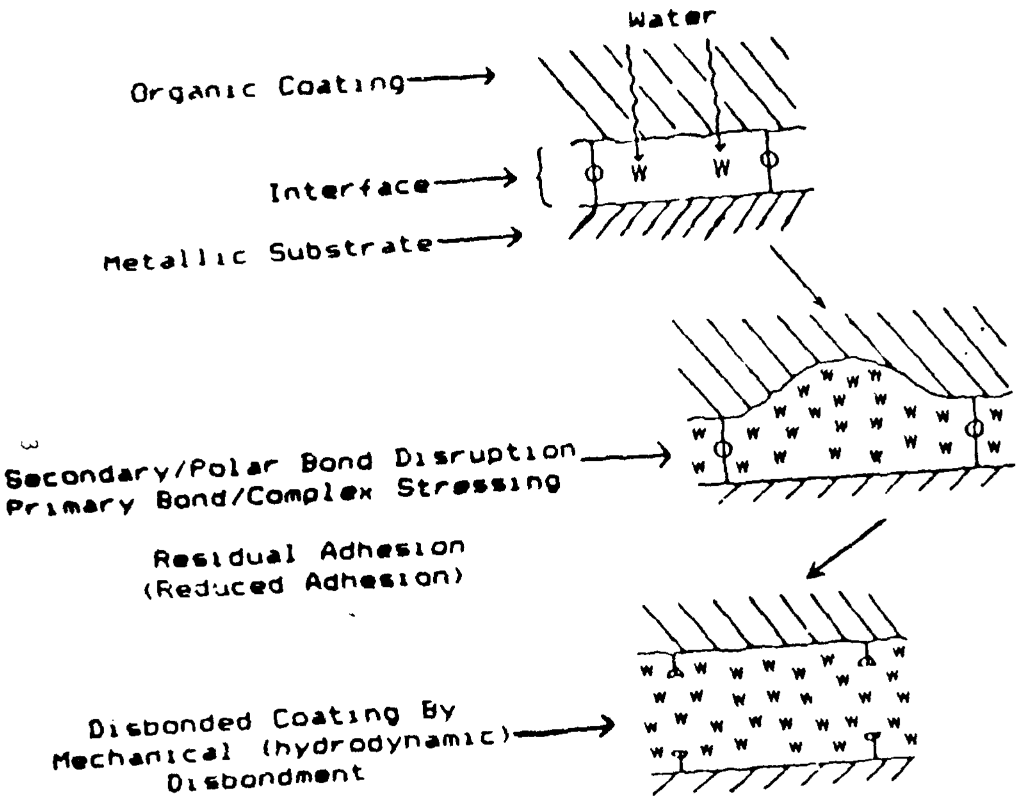
1. Introduction

Organic coatings have long been used to protect materials against degradation from the environments to which they are exposed. They perform this task by providing a physical barrier against the hostile conditions and also, by chemical means, through reactive pigments and fillers within the coatings. In order to provide this protection, one of the most important properties of these coatings is adhesion of the film to the substrate. One problem plaguing these materials is that the adhesion of many organic coatings to metallic substrates is adversely affected by exposure to an aqueous environment. [1-7] Even exposure to high relative humidities has been shown to cause coating adhesion loss. [2] In most cases, the adhesion loss is reversible, at least to some degree, when the coating is allowed to dry. [1,2,4] The amount of adhesion recovery is dependent on the severity of exposure and the strength of the specific polymer/metal interactions. Cathodic delamination studies and coating blistering studies have shown a loss of coating adhesion coincident with the presence of water at the coating/substrate interface. [1-7] Using a tape pull-off test on the exposed coated area immediately after removal from the test solution or environment produces an area of coating removal that does not occur if the coating is allowed to dry. Coating blistering in an aqueous environment is not always reversible. In some cases, there is a loss of intimate contact between the coating and the substrate which prevents the adhesion recovery. Various mechanisms to describe this phenomenon have been proposed in the literature. [2,8-12] Recently, Leidheiser and Funke proposed a chemical/hydrodynamical model to explain the mechanism behind this water disbondment phenomenon. [2]

The adhesion of polymeric coatings to metal substrates has two origins: mechanical and chemical. The mechanical adhesion of a paint is related to the type of anchor pattern it forms with the surface of the substrate. This anchor pattern is based on the physical interlocking of the coating with the surface oxide. Surface roughness/porosity and polymer wettability of the substrate are some of the important properties that affect mechanical adhesion. [13-17] The chemical adhesion of a coating is based on the type of chemical bonding between the two materials. The bonds can be either primary bonds/complexes or secondary London dispersion or acid/base bonds. [15-18] The type of surface oxide, substrate cleanliness, type of coating, specific coating/substrate interactions and cure conditions (i.e. temperature, environment, etc.) all affect the type of chemical bonding formed.

Leidheiser [2] proposes that when a coating/substrate system is exposed to an aqueous environment, water diffuses through the coating to the substrate interface under a concentration gradient. The water molecules move through pores and capillaries in the coating and accumulate at pre-existent unbonded areas at the coating/substrate interface. These unbonded areas have to be of sufficient size to allow condensation of the water molecules and can be the result of residual air voids left after coating application, surface contaminants, pre-existent physically or chemically absorbed water or dynamic voids resulting from the making/breaking of surface bonds by segments or polar groups in the polymer. The existence of a discontinuous or continuous liquid phase of water has been demonstrated by many authors and is summarized by Leidheiser and Funke. [2] Water continues to accumulate at the interface through osmotic forces; and these disbonded areas grow laterally. These forces are affected by electrolyte activity, polymer porosity and temperature gradients. During lateral growth, water molecules displace the polymer molecules by exerting a peeling force, due to their increased volume. This hydrodynamic force disrupts the chemical bonding in these areas and leads to coating adhesion loss. This phenomenon is illustrated in Figure 1. The rate of adhesion loss is determined by the resistance of the interface to these increasing water volumes. Many factors affect the wet adhesion loss of coating/substrate systems. The most important of these are also shown in Figure 1.

The present investigation characterized the water disbondment nature of 20 coating/substrate systems using a water immersion adhesion test. In addition, the interfaces of selected systems were also characterized using an FTIR spectroscopy technique; and the results of both test methods were correlated with the proposed model.



FACTORS AFFECTING DISBONDMENT

coating
substrate
coating/substrate
surface preparation
solution pH
ion concentration
temperature

Figure 1. Mechanisms of Adhesion Reduction and Disbondment by Water. This Figure is a Modification of That Used by Leidheiser and Funke [2].

2. Experimental Procedures

2.1 Materials

The coating systems chosen for this investigation consisted of four polymeric materials which are listed in Table I. These materials were selected because they cover a wide range of adhesion qualities with respect to their types of chemical adhesion bonds (primary vs secondary). They were used as neat resins, in order to eliminate any effects due to pigmentation or any specific pigment-binder interactions. In addition, when applied to the substrates, they formed clear films which enhanced visual inspection during testing. Some specific properties of these materials such as water vapor transmission rates, chemical resistance properties, etc. [19,20] are listed in Table II.

The acrylic was a thermoplastic polymethyl methacrylate resin in toluene. When applied, this material forms a polymeric coating by means of solvent evaporation rather than by a chemical reaction. This material was force-dried in an oven at 100°C for 30 minutes prior to testing. The chemical adhesion of the resultant film is proposed to be based solely on secondary bonding.

The polybutadiene was used as a solution of a carboxy-terminated butadiene resin in petroleum distillates. After application, a clear yellowish film is formed by the oxidative cure of the butadiene resin in an oven at 200°C for 30 minutes. The cured polybutadiene film is proposed to form primary complexes with the surface oxides depending on the substrate to which it is applied. [21-24]

The silicone alkyd resin was a silicone-modified medium/long oil alkyd in a solvent blend of VM&P naptha, toluene and isobutyl isobutyrate. This material cures by an oxidative reaction and, after application, was allowed to age for a minimum of one week at room temperature prior to testing.

The urethane was produced by reacting a polyester polyol with hexamethylene diisocyanate, resulting in the formation of an aliphatic polyurethane coating. The solvents present in the raw materials were ethylene glycol monoethyl ether acetate and xylene. The coating was allowed to cure by a polyaddition reaction at room temperature for a minimum of one week prior to testing.

Five metals were selected for evaluation in this adhesion study: aluminum, copper, steel, nickel and lead. Metallic

TABLE 1 RESIN SYSTEMS INFORMATION

RESIN TYPE	CHEMICAL NATURE	TRADE NAME/ MANUFACTURER	% SOLIDS	SOLVENT SYSTEM
THERMOPLASTIC ACRYLIC	METHYL METHACRYLATE	ACRYLOID B-66 ROHM AND HAAS	50	TOLUENE
POLYBUTADIENE	CARBOXY TERMINATED BUTADIENE	BUDIUM E.I. DUPONT CO	56	PETROLEUM DISTILLATES
SILICONE ALKYD	SILICONE MODIFIED MEDIUM/LONG OIL ALKYD	385-50E McCLOSKEY VARNISH CO.	50	VM&P NAPTHA, TOLUENE AND ISOBUTYL ISOBUTYRATE
POLYURETHANE	POLYESTER POLYOL/ DIISOCYANATE	DESMOPHEN 651-A-65	65	EGMEEA*
		DESMOPHEN 670-90	90	EGMEEA
		DESMODUR N-75	75	EGMEEA AND XYLENE

*EGMEEA = ETHYLENE GLYCOL MONO ETHYL ETHER ACETATE

TABLE II RESIN SYSTEM AND FILM PROPERTIES

RESIN TYPE	THINNING SOLVENT	FILM FORMING REACTION [20]	WVTR # (mg/cm2/hr)	ALKALI [19] RESISTANCE	ACID [19] RESISTANCE	WATER [19] RESISTANCE
THERMOPLASTIC ACRYLIC	CELLOSOLVE ACETATE	SOLVENT EVAPORATION	1.0 E-04	FAIR	FAIR	FAIR
POLYBUTADIENE	MIL-T-81772*	OXIDATION HEAT CATALYZED	0.5 E-04	EXCELLENT	EXCELLENT	EXCELLENT
SILICONE ALKYD	ETHYL ACETATE	OXIDATION ROOM TEMP. AIR	0.45 E-04	POOR	FAIR	GOOD
POLYURETHANE	MIL-T-81772*	R. T. ADDITION POLYMERIZATION	0.46 E-04	GOOD	FAIR	GOOD

*MIL-T-81772 IS A BLEND OF MEK, BUTYL ACETATE, TOLUENE, XYLENE AND PROPYLENE GLYCOL METHYL ETHER ACETATE

#WVTR'S WERE DETERMINED USING ASTM STM# D1653-72 WITH A ONE WEEK EXPOSURE PERIOD test coupons, 2.54 cm x 3.81 cm, were used for the water immersion adhesion test. Glass microscope slides were also chosen as a substrate for evaluation in this test. For the FTIR - ATR analysis, thin metal films (≈50 to 100 A thick) were evaporated on carbon-coated glass slides.

2.2 Water Immersion Adhesion Test

The water immersion adhesion test was designed to provide information about the water disbondment of several coating/substrate systems that were exposed to various test solutions. The test was performed by totally immersing coated metal panels in the solutions followed by adhesion measurements on the test panels after different periods of time.

2.2.1 Specimen Preparation

The metal test specimens were wet sanded with 400 grit silicon carbide sand-paper to provide a relatively uniform surface roughness for evaluation. After abrasion, the specimens were wiped with a cloth soaked in toluene to remove any loose surface grit remaining from the sanding operation. A boiling solvent degreasing method was used to remove any surface oils or greases. This method consisted of placing the test coupons in four beakers of boiling solvents. The beakers contained mineral spirits in the first two, and 95% methanol and 100% methanol in the next two, respectively. Finally, they were kept in a desiccator until the coatings were applied. The glass microscope slides were solvent degreased by wiping them with tissues dampened with methyl ethyl ketone and isopropyl alcohol prior to coating application. The test coatings were thinned to 16 seconds in a Zahn #2 cup using the solvents listed in Table II and were applied to the substrates by conventional air-spray. Once cured, the edges of these specimens were sealed with wax to eliminate any edge effects during testing.

2.2.2 Test Method

The painted panels were placed in wide-mouth 4 ounce jars containing the electrolyte solutions. At periodic intervals, the specimens were removed from the jars and the coating surface was immediately dried. Adhesive tape was applied to the coating surface with firm pressure and the tape was removed with a quick pull. Both the time and amount of coating removed from the substrate were recorded. The failure time of the specimen was designated as the point at which 50% of the coating was removed from the substrate.

2.2.3 Test Conditions

For the water immersion adhesion test, several variables were selected for investigation. The variables for the test specimens were coating thickness and surface preparation. Film thickness of the coating on the metal coupons was 25 ± 5 microns for most of the tests. However, film thicknesses of up to 60 microns were also evaluated. The effect of surface preparation was investigated by testing some of the substrates in an as-received condition (no sanding). The solution parameters that were varied included pH, ion concentration and temperature. The test specimens were exposed to solution pH's which ranged from 2 to 12. The ion concentration was varied from distilled water to 1 molar solutions of NaCl. In addition, several solutions of the same pH were prepared from different components in order to determine any effects of ionic composition. Finally, the effect of solution temperature was evaluated by conducting some tests at both room temperature and at an elevated temperature.

2.3 Interfacial Analysis

Nondestructive analysis of the interfacial region of an intact polymer/metal system has long been a significant problem. Most analytical procedures used by researchers to study coating/substrate interfaces consist of separating the two materials and analyzing them individually. This information is extrapolated to characterize the nature of the intact system. Recently, however, a nondestructive technique has been developed at Lehigh University which analyzes an intact simulated polymer/metal interface. [21,22] This technique incorporates an internal reflectance Fourier transform infrared (FTIR) spectroscopy technique known as attenuated total reflectance (ATR) to perform the interfacial analysis of a polymer/metal specimen. Both the air/polymer interface and the metal/polymer interface of some of these systems were evaluated using this technique. This information provided an insight as to the nature of the polymer-metal interactions.

2.3.1 Specimen Preparation

Thin metal films were evaporated onto carbon-coated glass slides. The glass slides were first cleaned in a sulfuric / nitric acid solution, neutralized with a NaOH solution and solvent wiped with ethyl alcohol. Next, a layer of carbon was evaporated on the surface to act as a release agent for the metallic film. Then, a thin film of metal was evaporated at 10^{-6} Torr onto the surface of the slide. This film is estimated to be 50 to 100 Angstroms thick. Finally, the polymeric material was applied by means of a spin-coater and cured as stated previously. The resultant coating film was approximately 10 microns thick. After curing, the polymer/metal film was peeled from the glass slide; and specimens were cut from the film and mounted on foam supports using double-face adhesive tape. Two sets of specimens were made for each system: one set with the air/polymer interface showing and the other set with the metal/polymer interface showing (see Figure 2).

2.3.2 Test Method

A Mattson Sirius 100 Fourier Transform Infrared (FTIR) Spectrometer configured in the Attenuating Total Reflectance (ATR) mode was used to obtain the interfacial spectra. A KRS-5 prism was used in this investigation. The polymer interface of interest was placed against the prism surface and set into the ATR apparatus as demonstrated in Figure 3. The prism was cut at a 45° angle which produced a depth of penetration ranging from 0.5 to 4.0 microns depending on the wavelength. The iris of the spectrometer was set at 60% open and 100 scans were accumulated to give the resultant spectra. Dry air was pumped into the chamber during scanning and the resultant spectra were ratioed to the KRS-5 background spectrum to obtain the true sample spectrum. After both interfaces were scanned, the air/polymer spectrum was compared to the metal/polymer spectrum to determine any significant differences between them. The results from this comparison were used to determine if there were any specific interactions between the metal and the polymer.

2.3.3 Test Conditions

The infrared spectroscopic technique was used on six systems prepared from two polymers and three metals. Both polybutadiene and acrylic resins were investigated using copper, iron and aluminum as the substrate metals. These polymer/metal systems were also evaluated after immersion in distilled water for 120 hours. The water-exposed specimens were prepared to the point just before the coating/substrate combination was peeled off the glass substrate. The glass slide was submerged in a beaker of water and allowed to age for 5 days. Finally, the slide was removed and the remainder of the specimen preparation was performed. The samples were allowed to dry in a desiccator prior to obtaining the spectra.

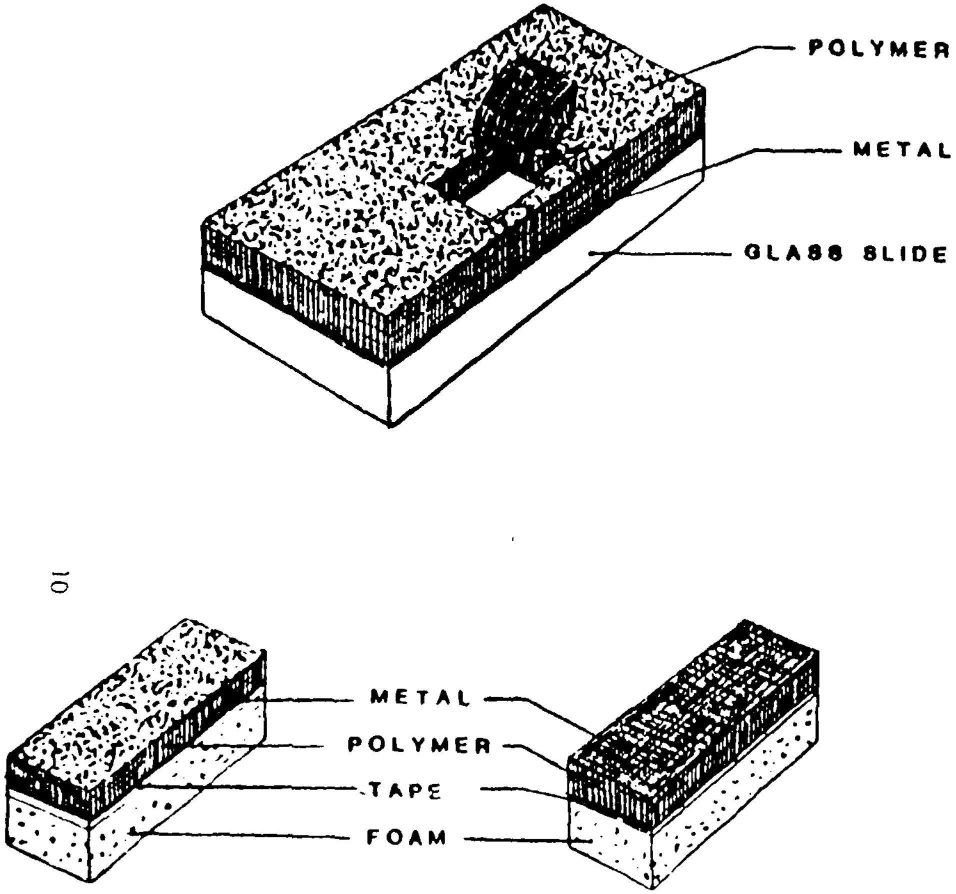


Figure 2. FTIR Test Specimen.

Figure supplied by P. Deck (22)

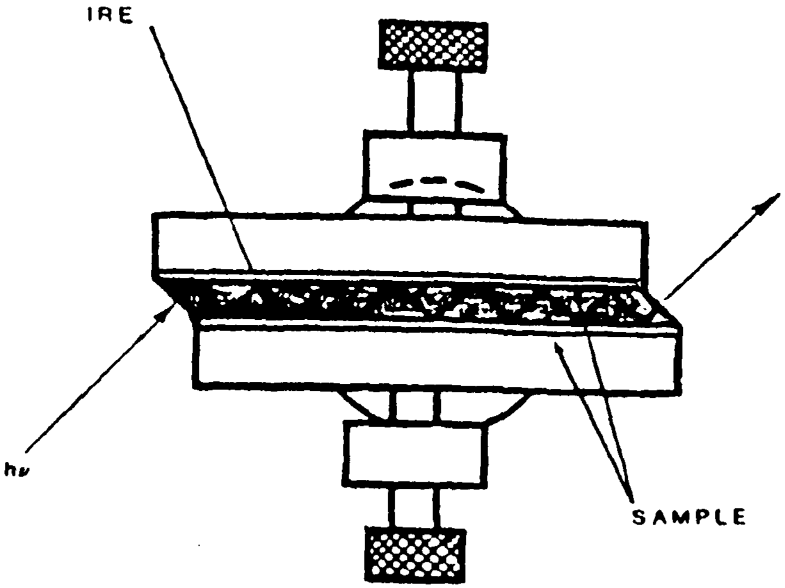


Figure 3. FTIR-ATR Test Fixture.

Figure supplied by P. Deck (22)

3. Results

The experimental test results fall into two main categories: mechanical adhesion test results and interfacial analysis results. The only exception is the water vapor transmission rates of these coatings which are shown in Table II. These rates were obtained according to the American Society for Testing and Materials, Standard Test Method # D1653-72, "Moisture Vapor Permeability of Organic Coating Films." The results are presented in the next two sections and will be discussed in detail in section 4.

3.1 Water Immersion Adhesion Test

The results for the water immersion adhesion test are presented in Tables III through XII. The values in the tables are the average of three replicates and represent the numbers of hours at which 50% of the coating was removed from the substrate in the tape pull test. Results for the replicates ranged up to 20% from the average value.

Failure times in the water immersion adhesion test for a 20 micron thick film of polybutadiene are summarized in Table III. These results cover all five metal substrates and solution pH´s ranging from 2 to 12. The failure area for polybutadiene was characterized by the initiation and growth of many small localized blisters that in time added up to meet the failure criterion.

Summarized test results for a 30 micron silicone alkyd coating under the same test conditions are presented in Table IV. The silicone alkyd film was cured for one week prior to performing these tests. Failure of this coating was characterized by the time dependent growth of blisters slightly larger than those for the polybutadiene system.

Table V covers a polyurethane coating on the five metallic substrates following a one week cure. The 20 micron thick film developed several large unbonded areas that grew together in most cases to reach the failure point. Although film disbondment was detected in the tape pull-off test, the disbonded coating remained intact for most of these tests. Therefore failure for these materials was based on the point at which 50% of the coating was disbonded. This phenomenon is believed to be due to the strong tensile strength and elasticity of polyurethanes.

Acrylic test results appear in Table VI and are based on an approximate film thickness of 60 microns. Again these results are for the same substrates and test conditions as the

TABLE III WATER IMMERSION ADHESION TEST RESULTS - POLYBUTADIENE
(HOURS TO COATING ADHESION FAILURE)

POLYBUTADIENE	SOLUTION pH				
SUBSTRATE	pH 2	pH 4	pH 7	pH 10	pH 12
COPPER	76	>170	>170	82	>170
ALUMINUM	120	>170	>170	>170	120
LEAD	34	>170	>170	24	>170
STEEL	24	18	168	24	6
NICKEL	110	113	144	>170	24

TABLE IV WATER IMMERSION ADHESION TEST RESULTS - SILICONE ALKYD
(HOURS TO COATING ADHESION FAILURE)

SILICONE ALKYD	SOLUTION pH				
SUBSTRATE	pH 2	pH 4	pH 7	pH 10	pH 12
COPPER	>170	138	>170	72	58
ALUMINUM	>170	>170	>170	>170	>170
LEAD	168	120	>170	168	>170
STEEL	10	14	24	24	16
NICKEL	3	3	5	4	3

TABLE V WATER IMMERSION ADHESION TEST RESULTS - POLYURETHANE
(HOURS TO COATING ADHESION FAILURE)

POLYURETHANE	SOLUTION pH				
SUBSTRATE	pH 2	pH 4	pH 7	pH 10	pH 12
COPPER	54	>170	>170	48	>170
ALUMINUM	>170	>170	>170	>170	>170
LEAD	70	70	168	48	>170
STEEL	1	12	16	24	10
NICKEL	1	3	2	1	6

TABLE VI WATER IMMERSION ADHESION TEST RESULTS - ACRYLIC
(HOURS TO COATING ADHESION FAILURE)

ACRYLIC	SOLUTION pH				
SUBSTRATE	pH 2	pH 4	pH 7	pH 10	pH 12
COPPER	120	>170	>170	72	>170
ALUMINUM	2	2	3	2	2
LEAD	>170	>170	>170	34	>170
STEEL	3	3	3	2	2
NICKEL	2	2	2	2	2

other three resins. The formation of a few blisters that grew rapidly together causing almost complete coating removal was characteristic of the acrylic failures.

Table VII contains the data for all four coatings on the glass substrate. Variables for these tests include film thicknesses and solution pH. In addition, results for duplicate specimens which were allowed to dry before the adhesion test was performed are presented in this table.

The effect of cure time was studied for the polyurethane/metal systems 4 months after they were prepared. In some cases the adhesion of these systems improved from the 1 week cure results. These data appear in Table VIII.

Acrylic-coated steel specimens were subjected to solution containing different ionic concentrations. Solutions of approximately the same pH, prepared from different ionic species were evaluated and these results are summarized in Table IX. Also, failure times for salt solutions ranging in concentration from 0 to 1 molar are listed in Table X.

Effects of surface preparation on two coating/metal systems were evaluated and this information appears in Table XI.

Finally, the effect of temperature was examined using the polybutadiene/nickel system. Two temperatures and five pH solutions were studied. These results are shown in Table XII.

3.2 FTIR-ATR Analysis

Internal reflectance spectral analysis was performed on two of the polymeric materials. The absorption spectra of these systems are presented in Figures 4-14.

Specimens with the polybutadiene coating on copper, iron and aluminum were prepared as specified in section 2.3.1. These specimens were mounted in the FTIR-ATR test fixture as illustrated in Figure 3 and the FTIR spectra were obtained. The air/polymer interface was analyzed before the metal/polymer interface was analyzed. Absorption spectra for both interfaces of the polybutadiene/copper system are shown in Figure 4. Comparison of these spectra indicates that there are some significant differences between the two interfaces. The air/polymer sample is more heavily oxidized than the metal/polymer sample. In addition, there is a peak in the carboxylate region of the metal/interface spectrum which is much more prevalent than in the air/interface spectrum. Figure 4 also shows the expanded carboxylate region for both

TABLE VII WATER IMMERSION ADHESION TEST RESULTS (GLASS)

COATING ON GLASS (THICKNESS-microns)	FAILURE TIME (HRS) pH 2	pH 4	pH 7	pH 10	pH 12	TYPE OF FAILURE	ADHESION* RECOVERY
POLYBUTADIENE (20)	>24(40%)	>24(5%)	>24(10%)	>24(25%)	>24(30%)	Spotty mainly from edges	YES
SILICONE ALKYD (5)	----	0.25	0.25	0.25	----	Initiated from medium to large spots that grew together	YES
SILICONE ALKYD (15)	0.25	0.25	1	0.25	0.50		YES
SILICONE ALKYD (45)	2	3	4	5.25	5.0		YES
SILICONE ALKYD(125)	----	----	>120	----	----		YES
POLYURETHANE (15)	0.5	0.75	1	1	0.5	Initiated from a few large spots growing together	YES
POLYURETHANE (30)	0.75	1.5	4	1.5	0.75		YES
ACRYLIC (10)	<5 min	<5 min	<5 min	<5 min	<5 min	Complete film disbondment	YES
ACRYLIC (25)	<5 min	<5 min	<5 min	<5 min	<5 min		YES

* Retested after coating was allowed to dry completely in a desiccant environment

TABLE VIII WATER IMMERSION ADHESION TEST RESULTS - POLYURETHANE/4 Mos.
(HOURS TO COATING ADHESION FAILURE)

POLYURETHANE	SOLUTION pH				
SUBSTRATE	pH 2	pH 4	pH 7	pH 10	pH 12
COPPER	168	>170	>170	48	>170
ALUMINUM	----	----	----	----	----
LEAD	70	168	168	168	>170
STEEL	----	----	168	----	----
NICKEL	126	126	126	70	6

TABLE IX ION CONCENTRATION EFFECTS (Same pH)

SOLUTION COMPOSITION	SOLUTION pH	TIME TO FAILURE (HRS) [ave. of 3]
50 ml of 0.025 M Borax & 0.9 ml of 0.1 M NaOH	9.14	168
50 ml of 0.025 M Borax & 2.0 ml of 0.1 M HCl	9.06	72
50 ml of 0.05 M Na Bicarbonate & 5.0 ml of 0.1 M NaOH	9.47	109

TABLE X ION CONCENTRATION EFFECTS (NaCl Solutions)

ACRYLIC ON STEEL (60 Microns)

SOLUTION CONCENTRATION	TIME TO FAILURE (min) [ave. of 3]
DEIONIZED WATER	17 + 10
0.001 M NaCl	99 + 15
0.01 M NaCl	75 + 15
0.1 M NaCl	92 + 15
1.0 M NaCl	95 + 15

TABLE XI SURFACE PREPARATION RESULTS

COATING-SUBSTRATE SYSTEM	SURFACE PREPARATION	FAILURE TIME (HRS)				
		pH 2	pH 4	pH 7	pH 10	pH 12
SILICONE ALKYD ON ALUMINUM (30 microns)	NO SANDING & SOLVENT WIPE WITH MEK	3.5	5.5	2.0	4.5	3.5
	SANDING (400 GRIT) & BOILING SOLVENT CLEANING METHOD	>170	>170	>170	>170	>170
POLYURETHANE ON STEEL (20 microns)	NO SANDING & SOLVENT WIPE WITH MEK	0.5	1	1.5	1.5	1
	SANDING (400 GRIT) & BOILING SOLVENT CLEANING METHOD	1	10	16	16 - 24	8
	WET SANDING & BOILING SOLVENT CLEANING METHOD	----	----	400*	----	----

*Polyurethane coating 75 microns thick

TABLE XII TEMPERATURE EFFECT RESULTS (POLYBUTADIENE ON NICKEL)

TEMPERATURE	FAILURE TIME (HRS) pH 2	pH 4	pH 7	pH 10	pH 12
21 C	110	113	144	170	<24
66 C	<24	<24	<24	<30	<24

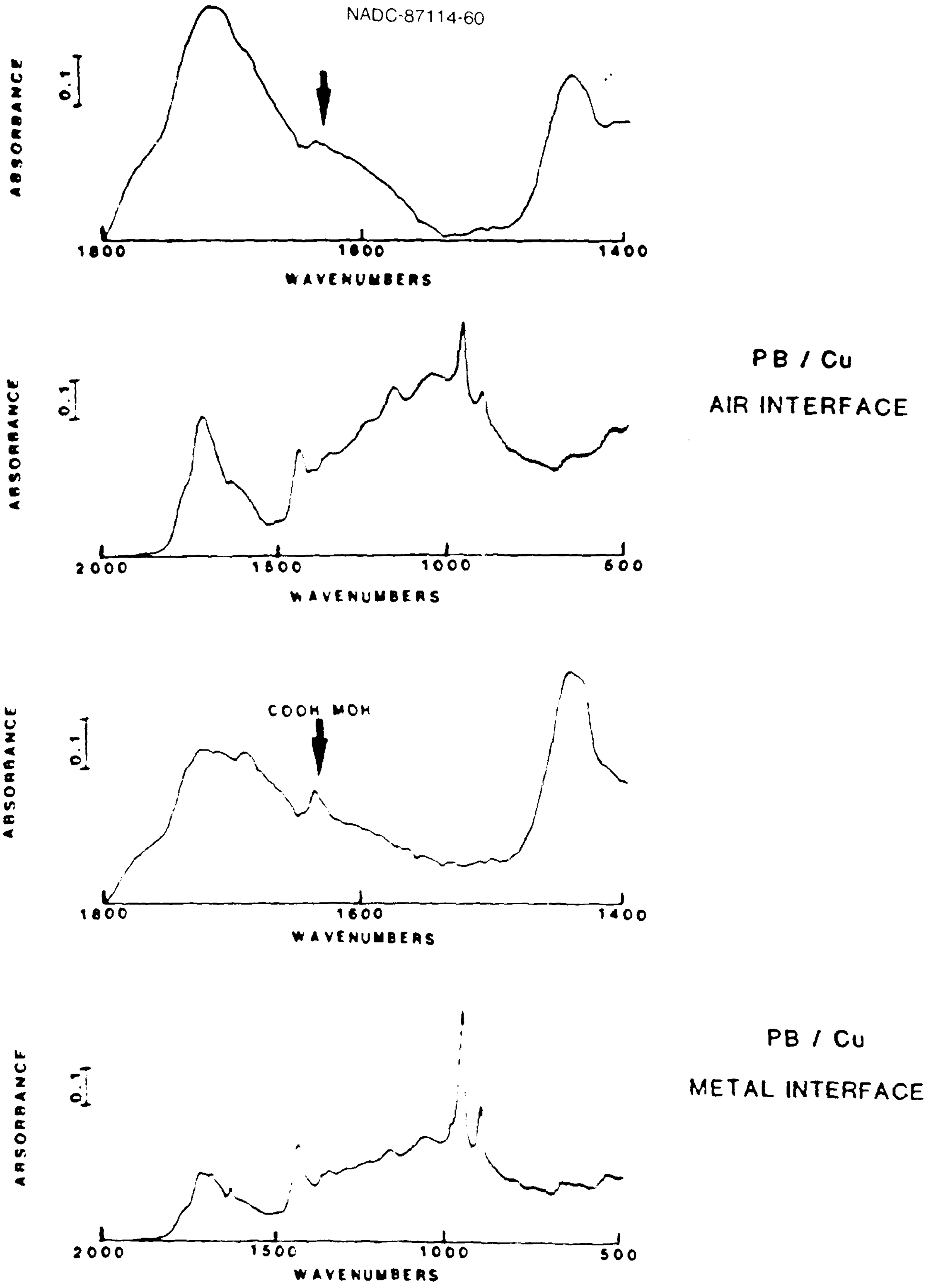


Figure 4. FTIR Spectra of Polybutadiene Copper System.

interfacial spectra. Further analysis of this peak indicates that it resulted from a complexed carboxylate species as outlined in the discussion section. The same phenomenon was apparent in the polybutadiene/aluminum and polybutadiene/iron spectra (see Figures 5 & 6).

Samples were prepared as specified in section 2.3.1 for the acrylic/copper, aluminum and iron systems; and spectra of both sample interfaces were obtained from the FTIR. The spectra for the air/polymer interfaces and the acrylic/aluminum and acrylic/iron interfaces show no significant differences in any of the peaks. These spectra are presented in Figures 7 & 8. The acrylic/copper interface when compared with the air/acrylic interface indicates the existence of a peak in the carboxylate region of the spectra as illustrated in Figure 9. These spectra were obtained from several samples and each time the same difference was noticed. To further examine this phenomenon, acrylic/copper test specimens were prepared at room temperature and the FTIR spectra of these samples were obtained (see Figure 10). Analysis of these data showed that the peak was not present for this system. These facts indicate that there is a copper catalyzed reaction occurring at the elevated temperature.

Polybutadiene/metal and acrylic/metal specimens were prepared to the point just prior to removal from the glass slide and then immersed in distilled water for 120 hours. Figures 11-14 contain both interfacial spectra for these samples.

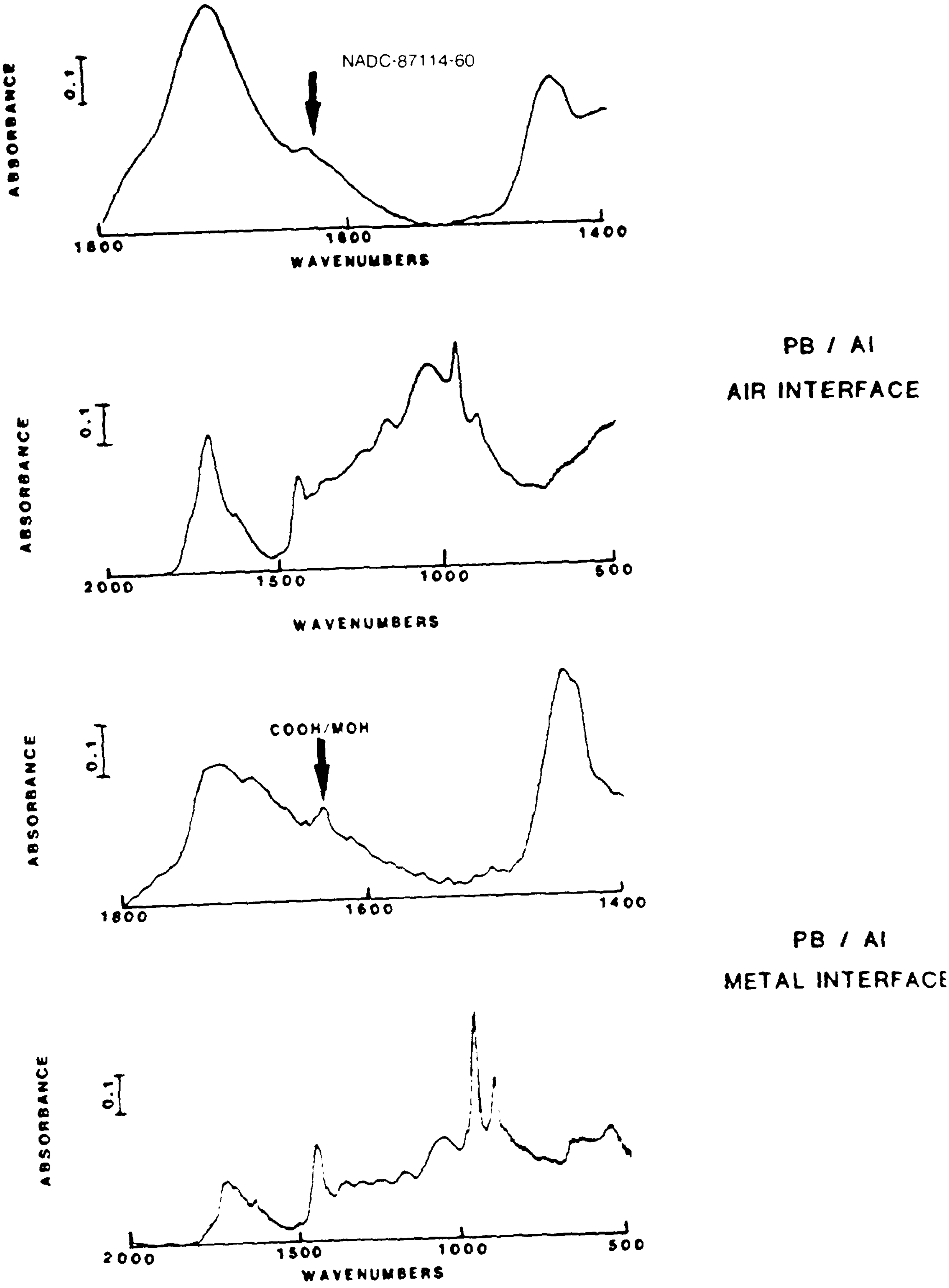


Figure 5. FTIR Spectra of Polybutadiene Aluminum System

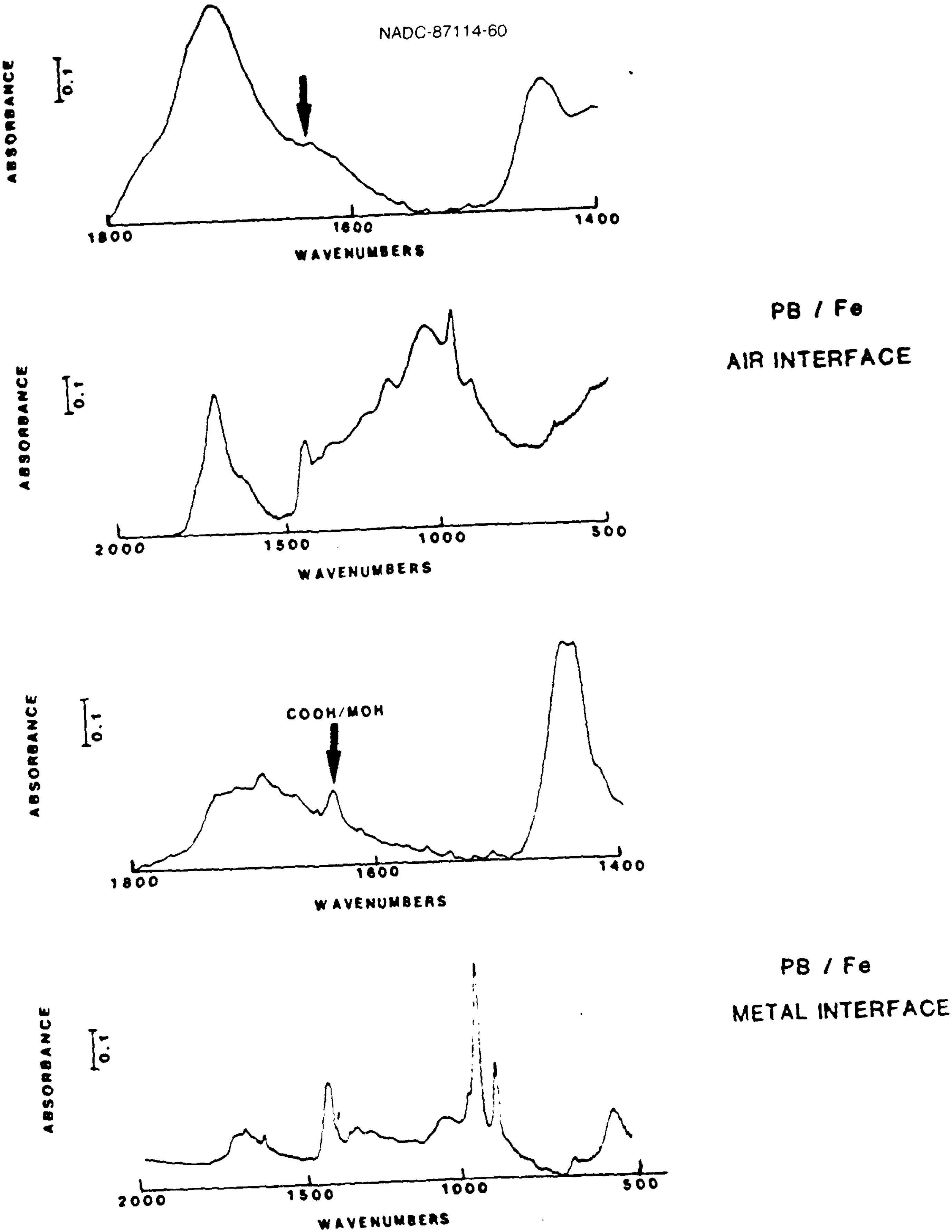


Figure 6. FTIR Spectra of Polybutadiene/Iron System.

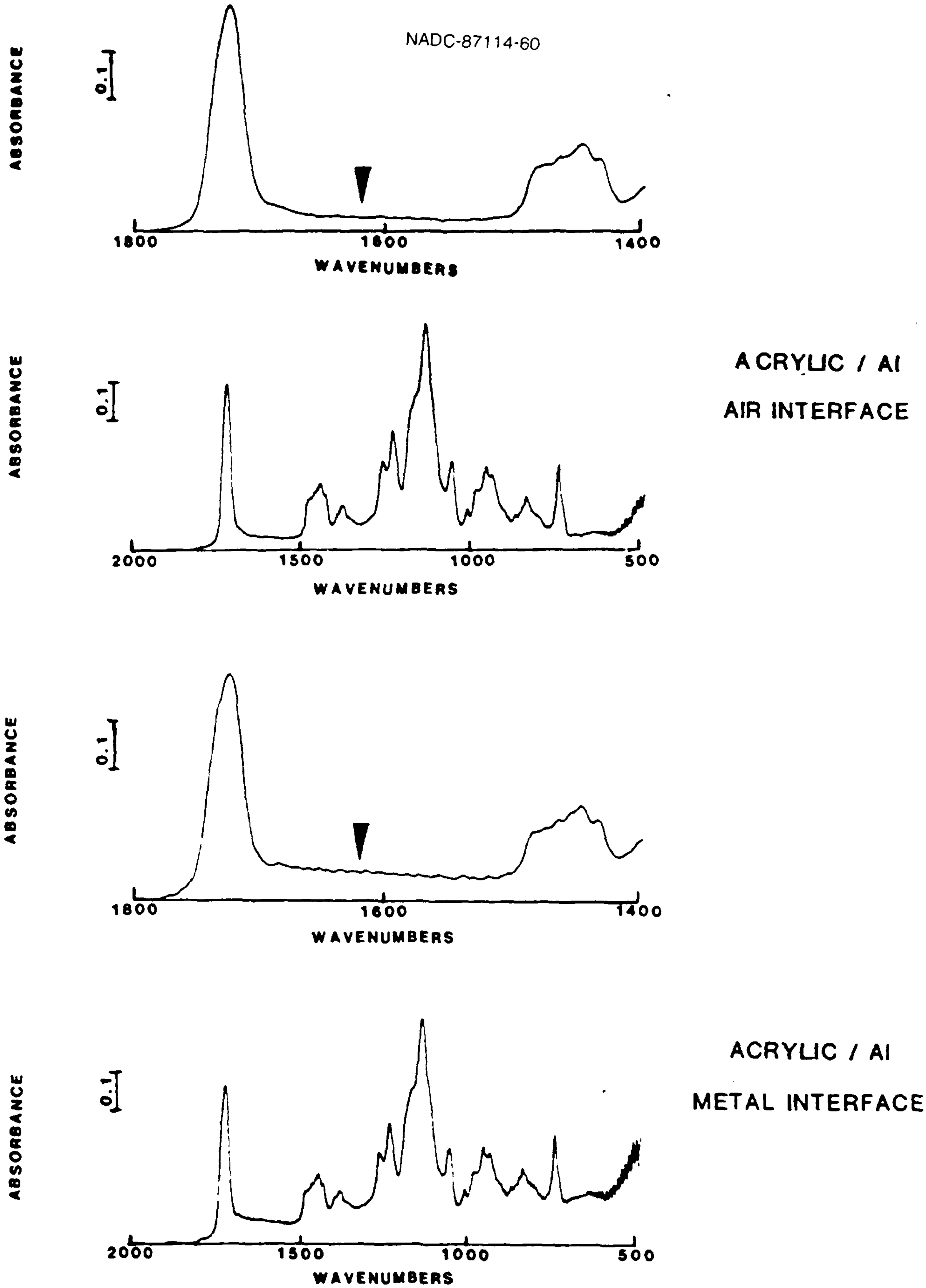


Figure 7. FTIR Spectra of Acrylic/Aluminum System.

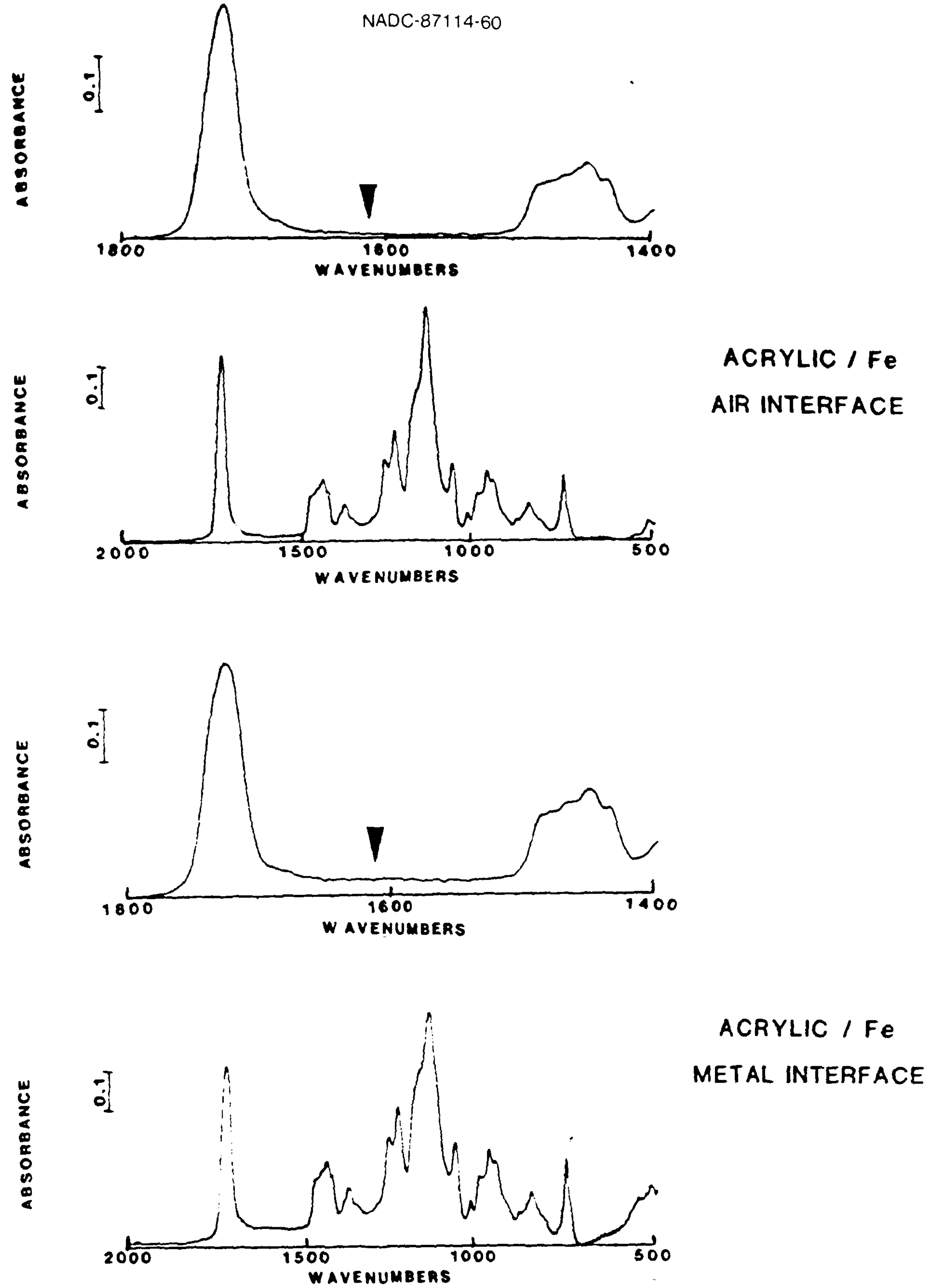


Figure 8. FTIR Spectra of Acrylic/Iron System.

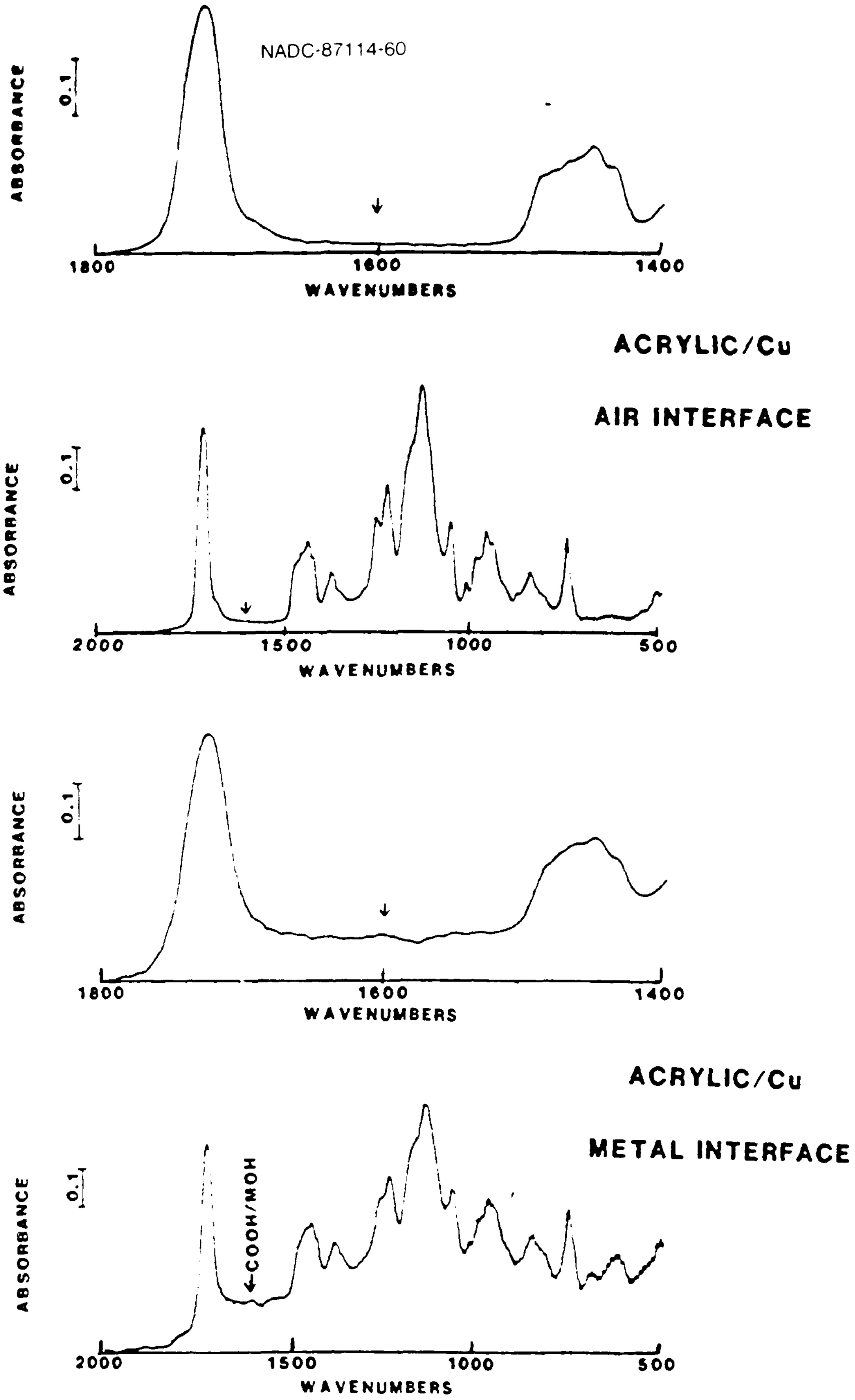


Figure 9. FTIR Spectra of Acrylic/Copper System.

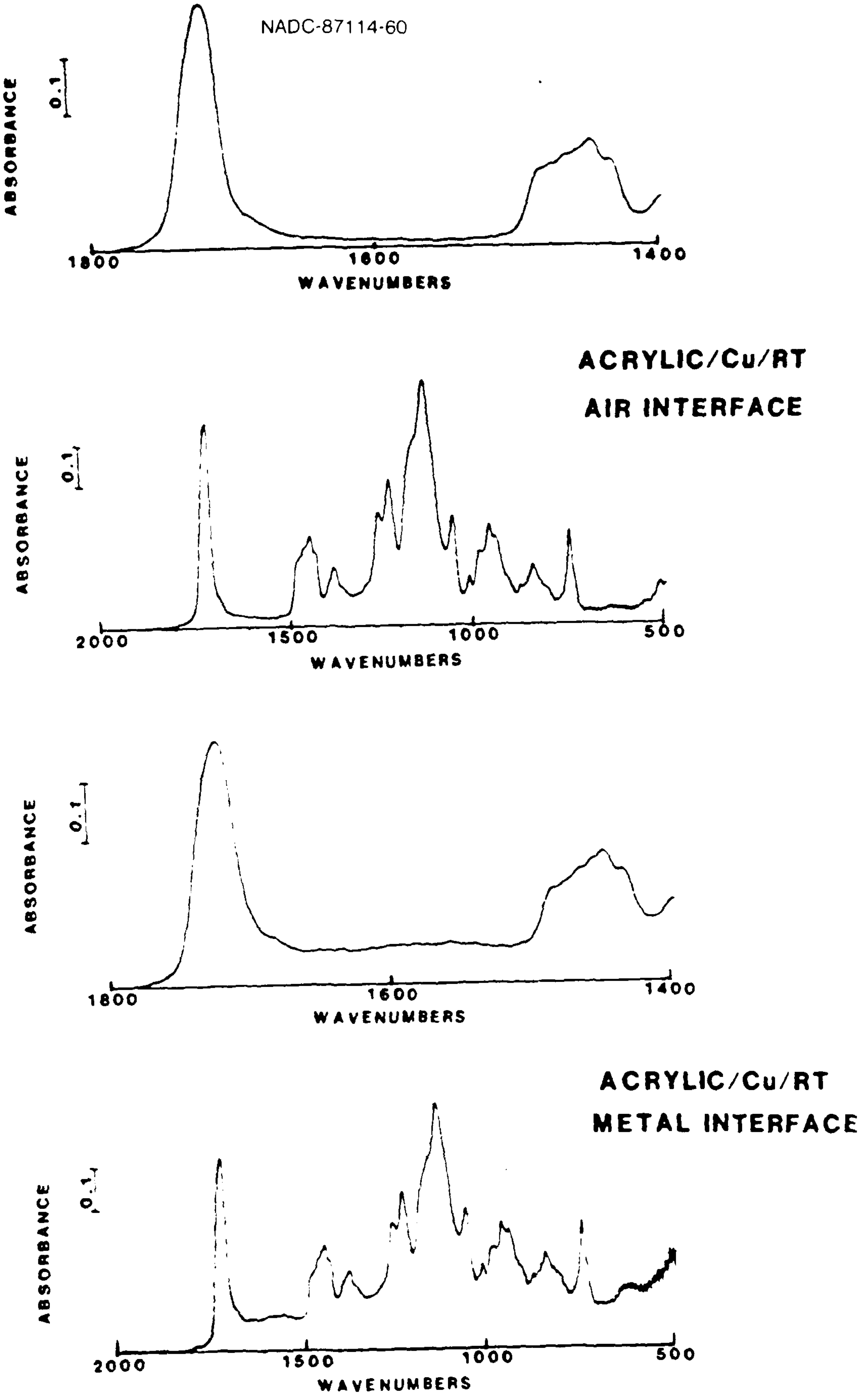
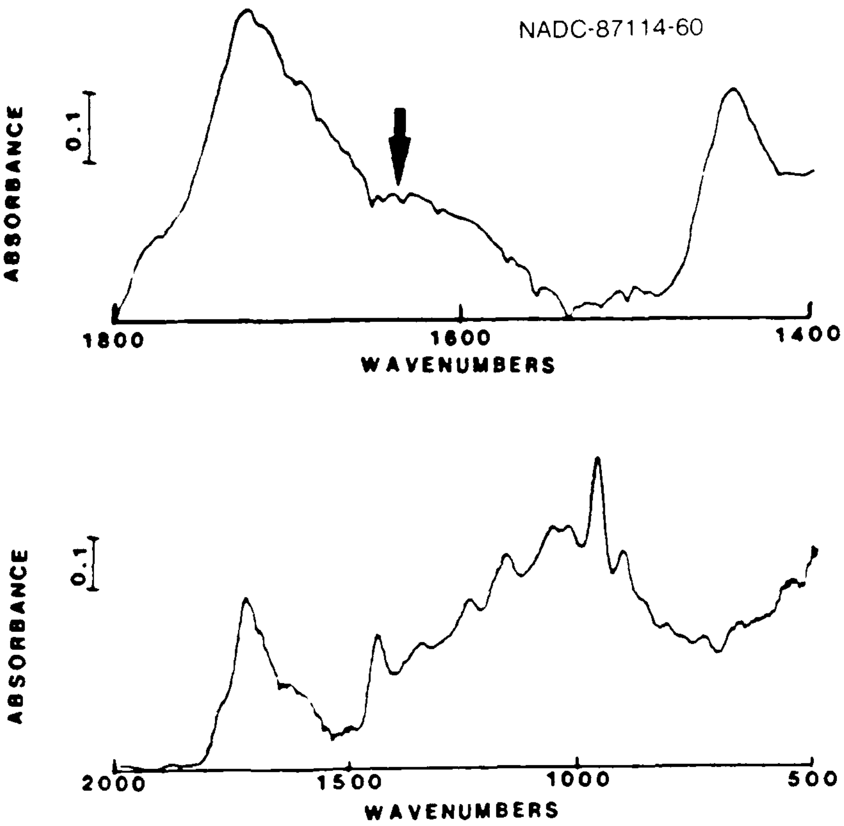
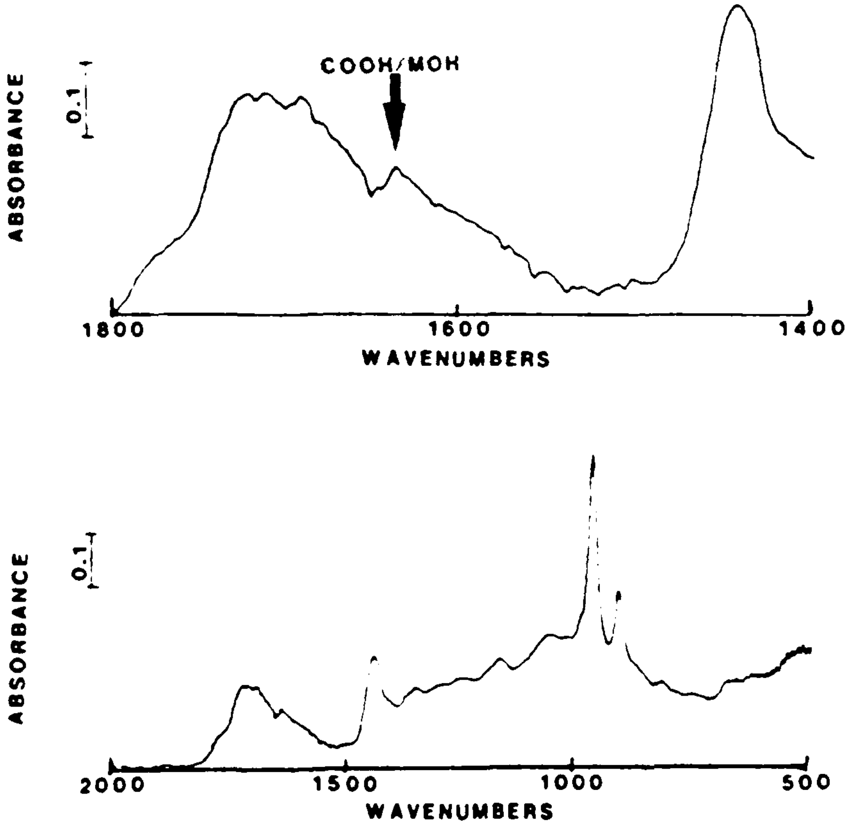


Figure 10. FTIR Spectra of Acrylic/Copper System Prepared At Room Temperature.



PB / Cu / WATER

AIR INTERFACE



PB / Cu / WATER

METAL INTERFACE

Figure 11. FTIR Spectra of Polybutadiene Copper System After Water Immersion.

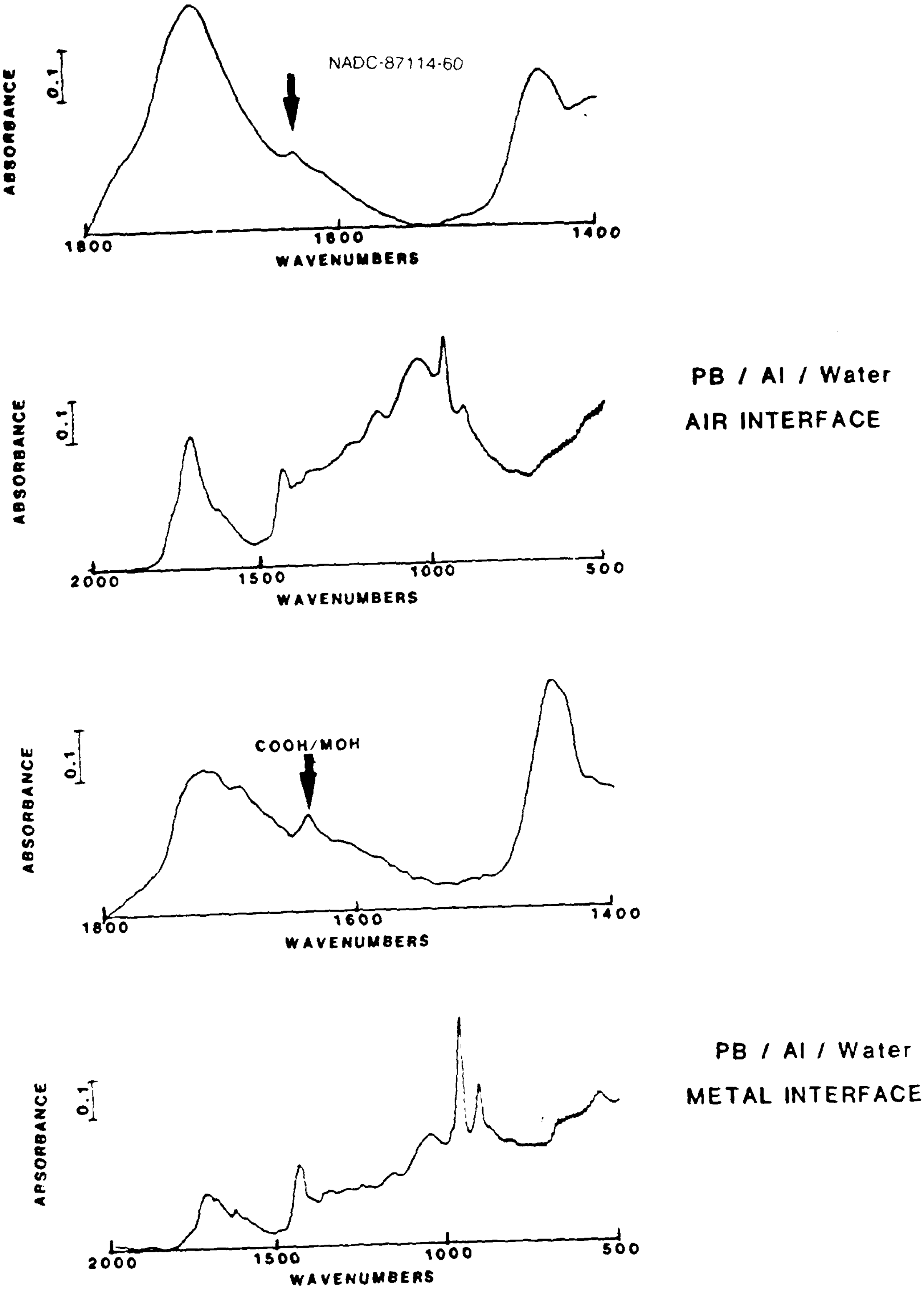


Figure 12. FTIR Spectra of Polybutadiene/Aluminum System After Water Immersion.

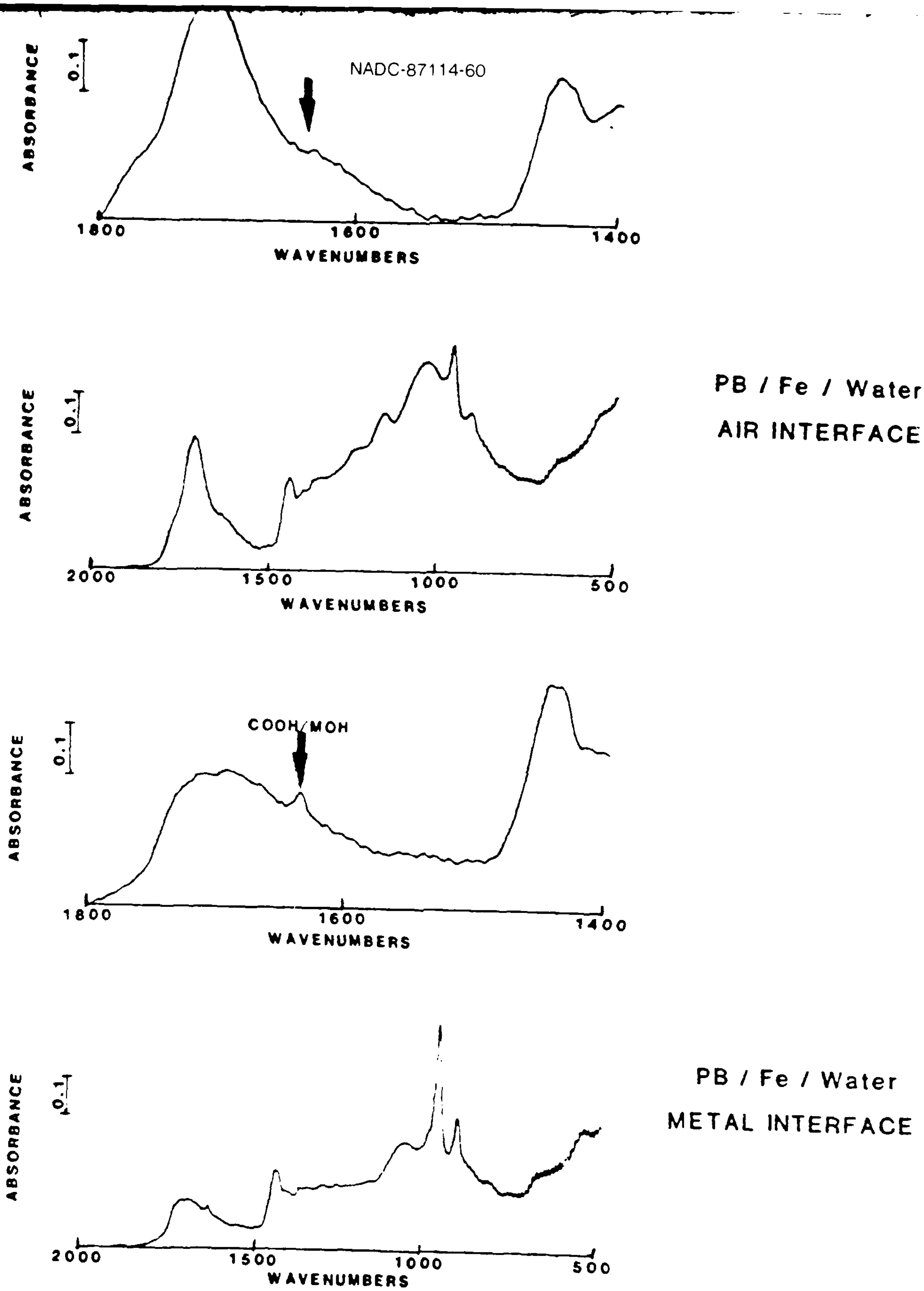
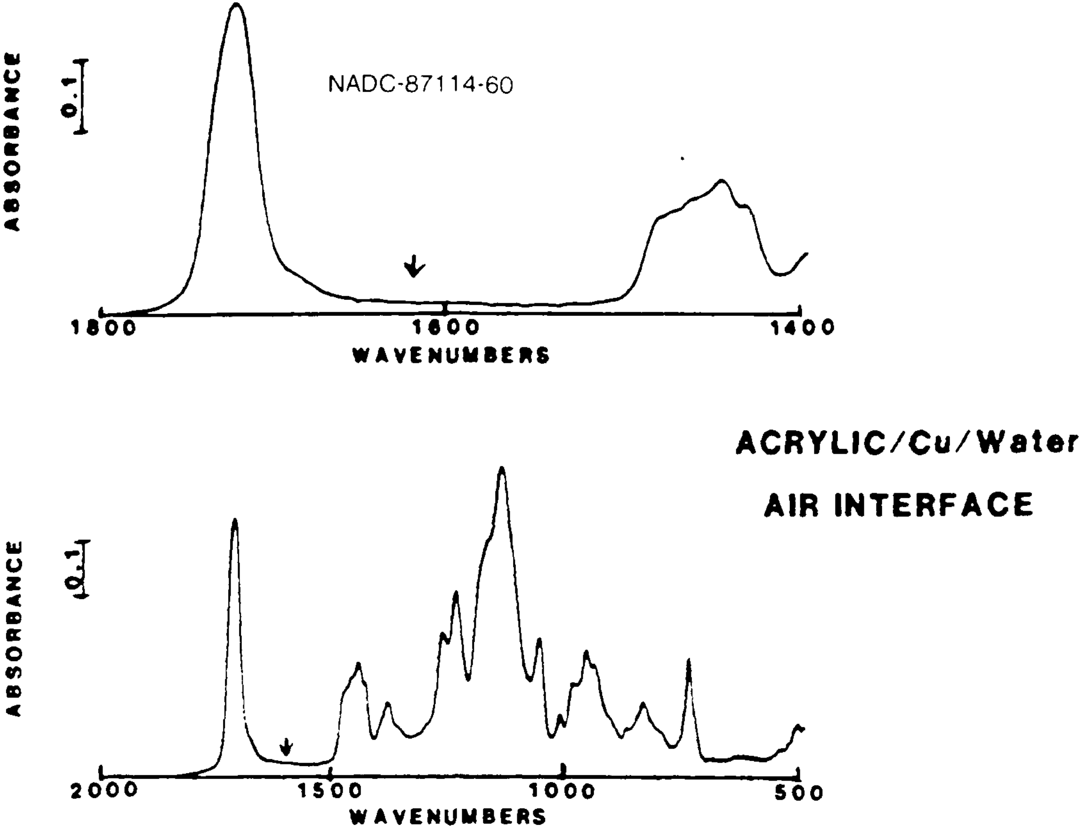


Figure 13. FTIR Spectra of Polybutadiene/Iron System After Water Immersion.


ACRYLIC/Cu/Water
AIR INTERFACE

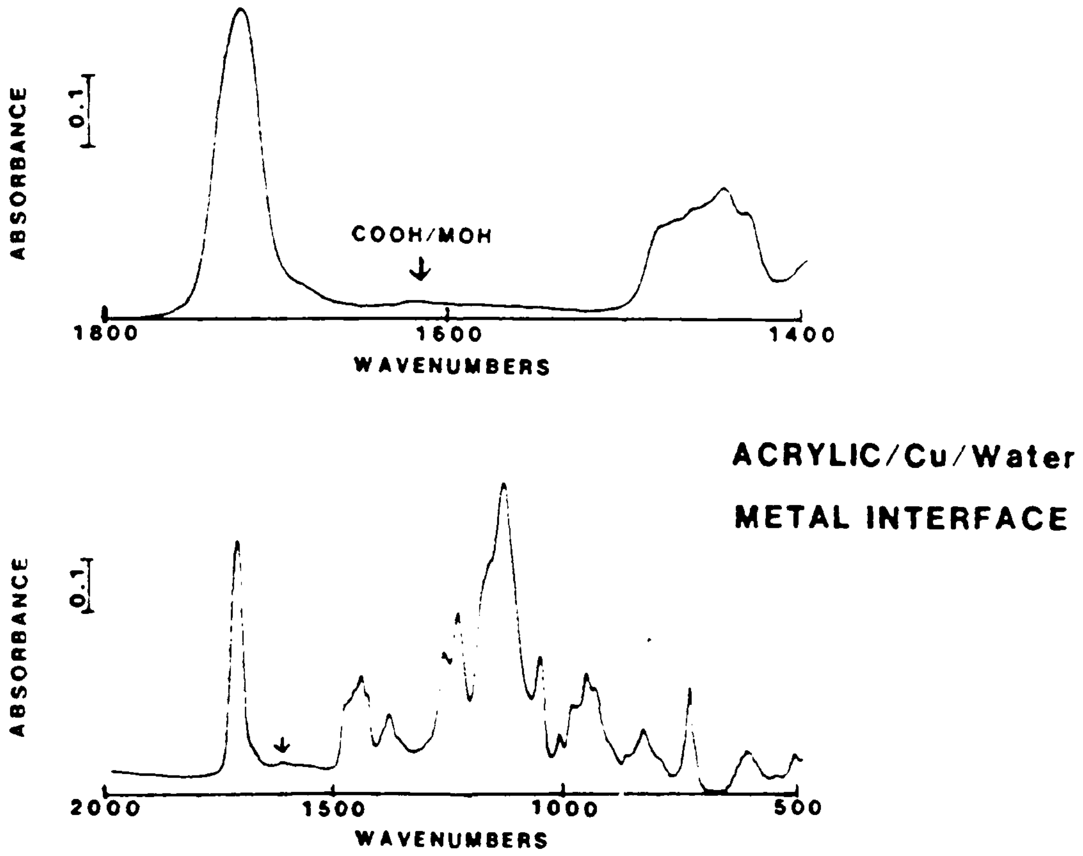

ACRYLIC/Cu/Water
METAL INTERFACE

Figure 14. FTIR Spectra of Acrylic/Copper System After Water Immersion.

4. Discussion

Many factors affecting the water disbondment of coating/substrate systems were identified from the results of this investigation. These effects are listed in Figure 2 and are elaborated on in section 4.1. Also in this section, the disbondment trends and specific affects developed throughout this testing program are compared with the proposed model for coating disbondment along with the reported results from other researchers. Discussion of the interfacial analysis results, their interpretation and their relationship to the proposed model is presented in section 4.2.

4.1 Discussion of Significant Effects.

The individual materials in the coating/substrate system play a significant role in the resistance to wet adhesion loss of the system. Coating selection plays a critical part in the water disbondment nature of the system. Differences in adhesion performance were evidenced when all other test conditions were kept constant and only the coating was varied. An example highlighting this effect can be seen by looking at the results for the various polymeric films coated on steel coupons and immersed in pH 7 test solutions. Polybutadiene failure occurred after 168 hours of exposure and was produced by the formation of many small localized spots of adhesion loss that eventually added up to meet the failure criterion. The silicone alkyd material which failed after 25 hours of exposure, resulted from the initiation and growth of disbondment areas larger than those of polybutadiene. Polyurethane failure occurred after 15 hours of immersion and was resultant from the growth of a few spots into large disbonded areas. Finally, the acrylic film was completely disbonded from the substrate in less than 3 hours. For this coating, once adhesion loss was initiated, it spread rapidly through the interfacial region. Data for this example are presented in Table XIII. Walker [25] also detected this effect in his studies of rates of adhesion loss under water immersion conditions. The same relative order of performance for coating systems similar to those used in this investigation was obtained. Comparison of performance results are outlined in Table XIV.

The type of substrate selected also plays an important role in the adhesion properties of the system. Tests conducted where the substrate was the only condition varied, showed a wide range of results for all coatings studied. Table XV contains the data from water immersion adhesion tests in a pH 7 solution for polyurethane-coated substrates. Systems with copper and aluminum withstood 170 hours of immersion without failure. The coating on lead lasted 168 hours before failure but showed good resistance to wet adhesion loss. Polyurethane on steel performed poorly and

TABLE XIII COATING EFFECTS

COATING ON STEEL	# HRS BEFORE ADHESION FAILURE	TYPE OF FAILURE
POLYBUTADIENE	170	VERY SPOTTY (SMALL)
SILICONE ALKYD	25	MEDIUM TO LARGE SPOTS
POLYURETHANE	15	LARGE SPOTS
THERMOPLASTIC ACRYLIC	3	ALMOST COMPLETE FILM FAILURE

TABLE XIV COMPARISON OF COATING PERFORMANCE

WALKER [24]		SPADAFORA	
COATING	RATE OF ADHESION LOSS	COATING	# HRS BEFORE ADHESION FAILURE
THERMOSETTING ACRYLIC	SLOW	----	----
STYRENE/ BUTADIENE	SLOW	POLYBUTADIENE	170
LONG OIL ALKYD	FAST	SILICONE ALKYD	25
POLYURETHANE	VERY FAST	POLURETHANE	15
----	----	THERMOPLASTIC ACRYLIC	3

lasted only 16 hours. While nickel and glass were the worst substrates, failing in only about 2 and 1 hours, respectively. The affect of substrates on coating interactions was demonstrated by Cullis and Laver [26]. Their study looked at the activity of the metal oxide in catalyzing the oxidation reaction of polybutadiene. Metal oxide powders were coated with polybutadiene and then analyzed using thermogravimetric tests. The minimum temperature at which the oxidation reaction occurred was recorded for each oxide. These data were interpreted in terms of the lower the temperature required for onset of oxidation, the more active the metal oxide was. Table XVI shows good correlation between the relative ranking of the oxide activity as determined by Cullis and Laver and the performance of the substrates in this investigation. In another research program, Walker [27,28] examined the effects of water spray on the adhesion of polyurethane using a tensile adhesion test both before and after exposure. Again, similar qualitative results were obtained by both researchers as evidenced in Table XVII.

Specific coating/substrate interactions can affect the water disbondment nature of a given system. A summary of this effect showing the failure times for all coating/metal systems in pH 7 test solutions is presented in Table XVIII. Here, coatings that perform well on one substrate, sometimes react differently on another. Similar results are true for substrates with different coatings. The strength and durability of the interfacial interactions varies depending on the system being tested.

As reported in Table XI of the results section, the surface preparation of the substrate can dramatically extend the adhesion life of a system. Increasing surface roughness improves mechanical adhesion between the materials, prolonging the wet adhesion failure of the system; although it does not prevent disbondment. Failures for roughened specimens under different exposure conditions still occurred in the same relative order, only at a much later times. This same trend was reported by Walker [27] who studied degreased and grit-blasted substrates.

Systems subjected to different solution pH's exhibited changes in their wet adhesion loss nature. One trend noted in this investigation was that adhesion performance improved for some systems as pH increased from values in the acidic range (pH 2-4) to neutral pH's and even into the alkaline range. However, in the high alkaline region the performance began to drop off significantly. Data showing this trend are summarized in Table XIX. Koehler [29] studied the effect of pH on organic coatings disbondment. One series of tests exposed steel specimens coated with polybutadiene to distilled water ($\approx$pH 7) and an ammonium hydroxide solution. Coating disbondment occurred for the alkaline exposed specimen in 4 hours; whereas, the distilled water specimens exhibited no

TABLE XV SUBSTRATE EFFECTS

SUBSTRATE COATED WITH POLYURETHANE	TIME TO ADHESION LOSS pH 7 (HOURS)
COPPER	>170
ALUMINUM	>170
LEAD	168
STEEL	16
NICKEL	2
GLASS	<1

TABLE XVI COMPARISION OF SUBSTRATE RESULTS

METAL OXIDE ACTIVITY CULLIS/LAVER	BEST OVERALL ADHESION SPADAFORA	
CoO		
Cr O		
CuO (varied)	Cu	VERY CLOSE
ZnO	Pb	
Al O	Al	
SnO		
NiO	Ni	
Fe O	Fe	
Cu O		

TABLE XVII MOSITURE EFFECTS ON POLYURETHANE ADHESION

WALKER [27,28] TENSILE ADHESION TESTS AFTER WATER SPRAY EXPOSURE

SUBSTRATE	INITIAL ADHESION	EXPOSURE EFFECT ON ADHESION
COPPER	GOOD ADHESION	NO EFFECT ON ADHESION
ALUMINUM	FAIR ADHESION	SLIGHT INCREASE IN ADHESION
STEEL	FAIR ADHESION	DECREASE IN ADHESION PERFORMANCE

SPADAFORA WATER IMMERSION ADHESION TEST (pH 7)

SUBSTRATE	TIME TO ADHESION LOSS (HOURS)
Cu	>170
Al	>170
Pb	168
Fe	16
Ni	2

TABLE XVIII COATING/SUBSTRATE INTERACTIONS (HOURS TO ADHESION FAILURE)

	COATING			
SUBSTRATE	POLYBUTADIENE	SILICONE ALKYD	POLYURETHANE	ACRYLIC
COPPER	>170	>170	>170	>170
ALUMINUM	>170	>170	>170	3
LEAD	>170	>170	168	>170
STEEL	168	24	16	3
NICKEL	144	5	2	2

TABLE XIX pH EFFECTS

	# HRS TO ADHESION FAILURE		
pH	POLYBUTADIENE ON NICKEL	POLYURETHANE ON STEEL	SILICONE ALKYD ON STEEL
2	110	1	10
4	113	10	14
7	144	16	24
10	170	$16 < x < 24$	24
12	$8 < x < 24$	8	16

adhesion loss after 4 days of immersion. These findings agree well with the results of polybutadiene/steel specimens in this test program.

Changes in the ion concentration of the test solutions can also alter the rate of adhesion loss. The addition of sodium chloride to distilled water in concentrations ranging from 0.001 to 1.0 molar, showed significant increases in failure times (Table IX). These increases in performance were attributed to the decreased thermodynamic activity of water in an ionic solution. In addition, similar pH solutions prepared from different ionic species produced changes in disbondment times for the acrylic/steel system.

Finally, increasing the solution temperature, accelerated the disbondment between the two materials. One possible explanation for this decreased performance is the increased rate of diffusion of water through the coating at the higher temperature. This resulted in shorter failure times for the system being tested as shown in Table XII. This temperature trend was also reported by Leidheiser in his paper presenting a proposed model for water disbondment of organic coatings.[2]

4.2 Discussion of FTIR Results

Comparison of the two interfacial spectra for a particular system gives information about the type of interactions occurring between the two materials. These data can then be used to interpret the nature of the adhesive bonds between the polymer/metal system.

Analysis of both spectra for all polybutadiene/metal systems shows significant differences between the two interfaces. Figure 15 shows spectra for both the air interface and the metal interface of the polybutadiene/copper system with the oxygen related peaks labeled. One difference in these spectra is the polymer/air interface is more heavily oxidized than the polymer/metal interface. This result is expected because oxygen which is present in excess at the air interface has to diffuse through the polymer to reach the metal interface. In addition, in the metal/polymer spectrum, there is a peak in the carboxylate region around 1600 wavenumbers which is much more prevalent than in the air/polymer spectrum. Figures 4-6 show the expanded carboxylate regions for both interfacial spectra of the polybutadiene/metal systems. Further analysis of this peak indicates that it resulted from a complexed carboxylate species as evidenced by Chan and Allaro [31]. Deck et al [22] used several analytical techniques, including this FTIR method to study coating/metal interfaces. Good correlation has been shown between the results from their different techniques to verify the existence of this complexed species. Polybutadiene was one of the polymers they investigated and their

ABSORBANCE

POLYBUTADIENE/COPPER SYSTEM

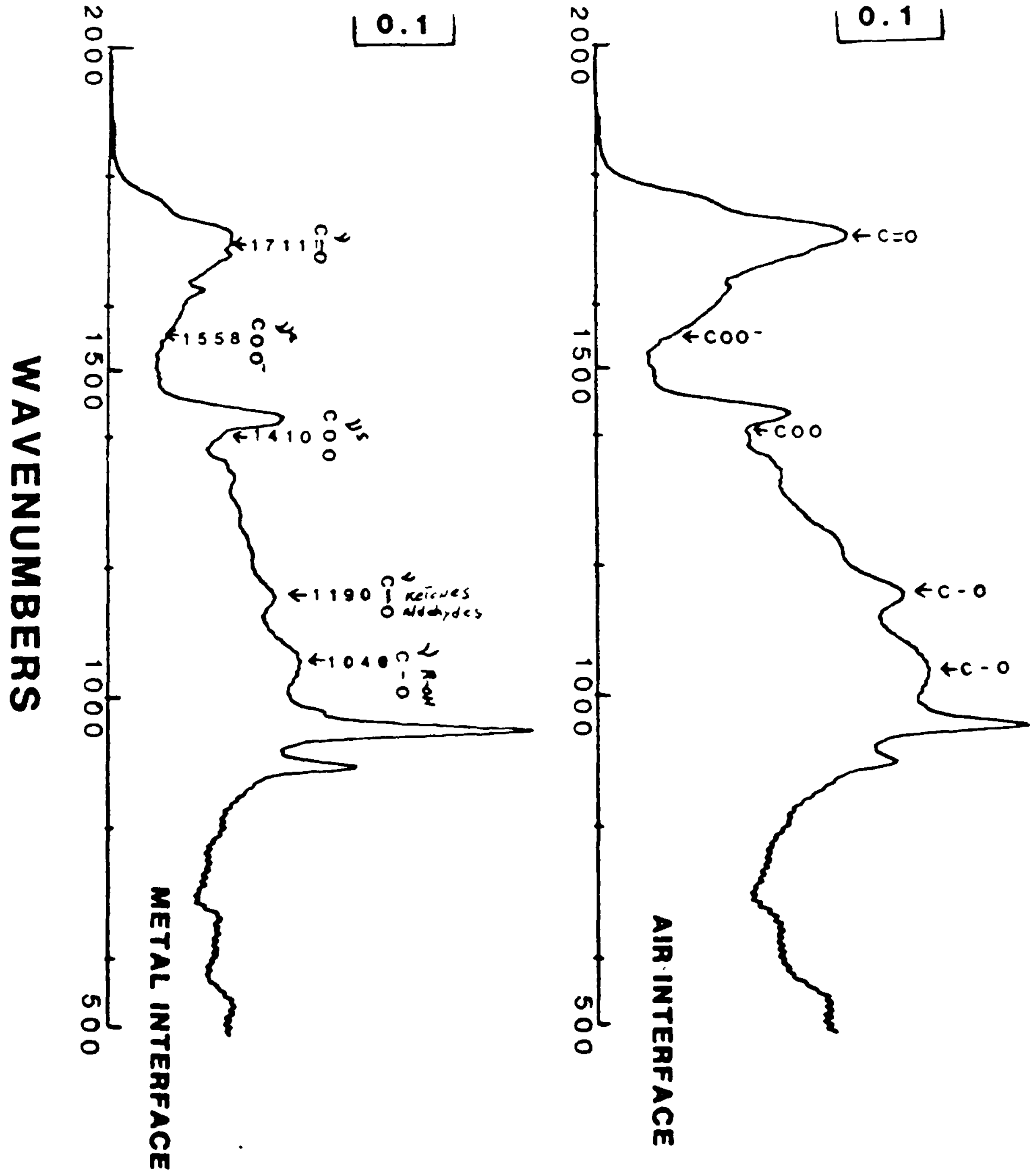


Figure 15. FTIR Spectra of Polybutadiene/Copper System With the Oxygenated Peaks Labeled.

interfacial spectra match the spectra obtained in this study. Other researchers such as Dickie [23,24], Salensky [30], Chan [31] and Francis [32] have reported similar types of primary interaction between polymers and metals using many different techniques. Again, polybutadiene-coated specimen performed the best overall in the water immersion adhesion tests. Also, the nature of the failure for polybutadiene which consisted of small localized areas of disbondment that resisted growth is indicative of primary interactions at the interface.

FTIR spectra for samples prepared from the acrylic resin with copper, aluminum and iron substrates were obtained. Analysis of the spectra for the air/polymer interfaces and the acrylic/aluminum and acrylic/iron interfaces (Figures 7 & 8) show no significant differences in any of the peaks. This result indicates that there are no primary chemical interactions between the acrylic polymer and aluminum and iron. This lack of interaction correlates well with the poor performance of these systems in the water disbondment tests. Once coating disbondment was initiated in these systems, it spread rapidly through the interface. The acrylic/copper interface when compared with the air/acrylic interface, however, shows the existence of a peak in the carboxylate region of the spectra as illustrated in Figure 9. Several spectra were obtained from replicate samples and each time the peak was present. This peak may have been generated by a copper catalyzed reaction during the drying process since it does not occur on any of the other acrylic spectra. In addition, the acrylic/copper system in the water immersion adhesion tests far out-performed that of the steel or aluminum systems. These facts indicate that there is some type of primary interaction between the acrylic polymer and the copper substrate which is not present in the other systems. To verify this finding, specimens of acrylic on copper were prepared but room temperature dried. Spectra for these samples did not show the peak in the carboxylate region (see Figure 10) which strengthens the theory that the peak represents a copper/temperature catalyzed species.

Polybutadiene/metal and acrylic/metal specimens prepared to the point just prior to removal of the system from the glass slide were immersed in distilled water for 120 hours. After exposure, specimen preparation was completed and the interfacial analysis was performed. Comparison of the polybutadiene/metal interface spectra, with and without water exposure, shows no significant differences between the two spectrum. If chemical disruption of the carboxylate complex occurred due to the presence of water, a peak would still be present in the carboxylate region, only shifted in position. Analysis of the water-immersed system spectrum shows no shifting of the carboxylate peak from the position for the unexposed specimens. The same analysis holds true for the acrylic/copper spectra. These data support the theory of hydrodynamic disbondment as opposed to chemical disbondment.

5. Conclusions/Summary

Many factors affect the water disbondment nature of organic coating/metal substrate systems. The individual materials in the coating/substrate system play a significant role in the resistance to wet adhesion loss of the system. Coatings that exhibit primary interactions with the substrate material have a much greater resistance to wet adhesion loss. Substrate oxides with higher activities tend to perform better in water disbondment tests. Specific coating/substrate interactions also affect the water disbondment nature of a given system. Coatings that perform well on one substrate, may react differently on another. Similarly, substrates may react differently depending on the coating.

The surface preparation of the substrate can dramatically extend the adhesion life of a system. Increasing surface roughness prolongs the wet adhesion failure of the system; although it does not prevent disbondment. Failures for roughened specimens still occur in the same relative order, only at much later times.

Solution pH, ion concentration and temperature can all change the resistance to water disbondment performance of coating/metal systems.

FTIR spectral analysis of all polybutadiene/metal systems showed significant differences between the two interfaces. The metal/polymer spectra show a peak in the carboxylate region around 1600 wavenumbers which correlates to a complexed carboxylate species. Polybutadiene performed the best overall in the water immersion adhesion tests, which correlates well with the presence of this type of species.

The acrylic resin on aluminum and iron systems exhibit no primary chemical interactions between the polymer and metal, which correlates well with the poor performance of these systems in the water disbondment tests. The acrylic/copper system showed the existence of a peak in the carboxylate region of the spectra indicating some type of primary interaction between the acrylic polymer and the copper substrate. This correlates well with the performance of this system in the water immersion adhesion tests.

Polybutadiene/metal and acrylic/copper specimens immersed in distilled water show no significant differences due to the exposure; thereby indicating no chemical disruption of the carboxylate complex. The data support the theory of hydrodynamic disbondment as opposed to chemical disbondment.

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