Research Report

KTC-91-7

Protective Coating Program

Final Report

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EXECUTIVE SUMMARY

This program consists of two primary segments: 1) installing an environmental monitoring station at the Toyota marshalling yard at Georgetown, Kentucky, and 2) conducting laboratory and field tests of paint and wax-coated painted specimens to assess the protection against acid rain damage afforded by a protective transient coating.

The monitoring station program objectives were:

1. Procure, install, and test an atmospheric deposition station;
2. Characterize the general atmospheric chemical environment;
3. Determine specific atmospheric chemical environment during open exposure of test specimens;
4. Develop a data base to estimate probability of severe acid deposition events; and
5. Conduct pH tests of rain samples on an event basis.

To meet the first set of objectives, researchers assisted Toyota personnel in selecting, installing, and operating a monitoring station (precipitation collection system) at the Toyota site. On-site analysis equipment was provided to allow Toyota personnel to conduct chemical characterization of collected samples. Researchers provided Toyota personnel with training to obtain and analyze the samples. During the start-up period between February and August 1990, researchers collected and analyzed samples from 46 precipitation events. Those data were compared with those taken at the Kentucky Acid Deposition Program site at Perryville, Kentucky. The data taken did not reveal the presence of any unusual atmospheric conditions. In August, 1990, Toyota personnel assumed complete operation of the monitoring station and data analysis equipment.

The testing program objectives were:

1. Determine effect of temperature and humidity on the ability of wax to protect vehicle finishes,
2. Determine period of time wax protects against acid rain, and
3. Determine mechanisms of acid rain interaction with wax and paint.

Four tests were performed to determine how well the protective transient coating (wax) protected against acid rain.

1. Cyclic evaporation tests - to simulate the effect of multiple acid rain events.
2. Laboratory soak tests - to simulate the effect of a single acid rain event followed by hot, dry conditions.
3. Humidity laboratory tests - to simulate the effect of a drop of rain remaining (and not evaporating) on a hot vehicle surface.
4. Field exposure tests - to simulate a single-drop evaporation followed by exposure at the Toyota marshalling yard.

A range of Ph values from 2.26 to 7.50 was covered and simulated as well as natural rains were used. Specimens of three colors, white, light blue, and dark blue were tested at temperatures of 110, 150, and 170 °F. The resulting damage was assessed visually and more than 2,000 specimens were tested.

The most typical acid rain damage is etching caused by corrosive attack to the paint by acids in the test solutions. That damage is revealed either as concentric rings or as random pits in the surface of the paint. In some cases, acid rain damage is revealed as surface deposits. That can be due to crazing of the paint surface, leaching of certain paint compounds, or depositions of solids from the acid rain solutions/particulate interactions. That damage can occur concurrently with etching.

Results for all laboratory tests, waxed and unwaxed indicate that acid rain damage is primarily a function of the pH of the acid rain solution (Appendix 2, Figure 27). The experiments conducted during this program reveal that the Yuma Industries **YUMAX SR-10** water based acrylic resin coating provides a measure of protection to the current paints used by Toyota Motor Corporation throughout the range of acid rain solutions tested (Appendix 2, Figure 28). The amount of protection decreases as the pH decreases. The coating appears to be satisfactory to prevent damage from moderately acidic rains and dews. However, the amount of acid rain protection does not appear to be significant when the pH is lower than 4.0.

In most tests, paint damage occurred due to the evaporation-to-dryness of the acid rain solutions. Evaporation appears to play an important role in the damage process.

The current practice of washing vehicles after acid rains having pH values less than 4.0 appears to provide some benefit. Laboratory testing shows that the benefit can be increased greatly by washing before an acid rain evaporates.

Test temperature, paint color, and test type all appear to affect the susceptibility of the paint to damage (Appendix 2, Figures 29-31). Most laboratory tests appear to be more severe than the field exposure tests. That should be taken into account when employing laboratory tests to determine paint or transient coating suitability.

Further work is recommended in three areas: 1) laboratory testing, 2) field testing, and 3) development of an early warning capability for the occurrence of severe air pollution events. Laboratory tests would include: 1) studying the effect of sulfate:nitrate ratio on acid rain damage, 2) investigating acid rain damage mechanisms, 3) determining the effect of transient coating thickness on protection from acid rain damage, 4) preparing formalized test procedures incorporating accelerated testing, and 5) performing statistically valid acid rain damage testing to quantitatively characterize the acid rain resistance of paint and wax. Field evaluation tests would include: 1) studying the effect of field exposure on transient coating acid rain resistance, 2) investigating the change in pH of rain drops during evaporation, and 3) performing extended field exposure tests to correlate field results with laboratory tests. Early warning capability work would include: 1) investigating recently developed real-time regional-scale meteorological prediction models, 2) developing an early warning capability for the occurrence of severe air pollution episodes at the Toyota marshalling yard at Georgetown, Kentucky, and 3) "tuning" the model based on actual weather patterns and acid rain activity experienced at the marshalling yard.

PROTECTIVE COATING PROGRAM

FINAL REPORT

prepared for Toyota-VPI
by
the University of Kentucky

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1. INTRODUCTION

1.1 Background

1.1.1 It is well known that acidic deposition from environmental pollution may cause damage to the finish of automobiles. The results of a recent large study by General Motors was reported in the December 1990 issue of the Journal of Air Waste Management (Appendix 1, Reference 1). The role of sulfates and nitrates and the need for a wetting event, such as rain or dew, are discussed. Rain, which is quite acidic, is not unusual in the Georgetown area and there is clearly a need to protect the finish on the cars stored in the marshalling yard. The protective coating now (1989 to present) being used was intended to protect mainly against industrial pollution such as iron particles which may be deposited on the car surfaces during rail transport.

1.1.2 In January, 1989, Toyota Motor Sales, U.S.A., Inc. requested that the University of Kentucky (UK) conduct a research program related to acid rain protection for vehicle finishes. In April, 1989, the University of Kentucky responded with a proposal for a research program. The program was initiated in May, 1989. Active research on the program was completed in December, 1990.

1.1.3 Three UK departments: 1) the College of Engineering - Mechanical Engineering Department, 2) the Kentucky Transportation Center (KTC), and the Center for Applied Energy Research (CAER) provided manpower and resources to conduct the needed research. The overall direction of the study was provided by Mechanical Engineering Department personnel. Laboratory and field performance tests of the wax and paint specimens were conducted by KTC personnel. CAER personnel assisted in establishing a monitoring station at the Toyota marshalling yard in Georgetown, KY. They also performed laboratory analyses of wax coatings and acid-damaged test specimens.

1.2 Objectives

1.2.1 The primary objective of this program was to evaluate the ability of the protective transient wax coating being applied to new Toyota automobiles in 1989 to protect the finish against acid rain damage. The coating, manufactured by Yuma

Industries Inc., **Yumax SR-10**, is a water-based acrylic resin. The program comprised two main segments. The first involved installing a monitoring station and the second involved testing of specimens furnished by Toyota.

1.2.2 Monitoring station objectives

1. Procure, install, and test an atmospheric deposition monitoring station;

2. Characterize the general atmospheric chemical environment;

3. Determine specific atmospheric chemical environment during open exposure of test specimens;

4. Develop a data base of acid deposition events; and

5. Conduct Ph tests of rain samples on an event basis.

1.2.3 Testing program objectives

1. Determine effect of temperature and humidity on the ability of wax to protect vehicle finishes,

2. Determine period of time wax protects against acid rain, and

3. Determine mechanisms of acid rain interaction with wax and paint.

1.3 Progress

1.3.1 The monitoring station objectives were accomplished on schedule and at considerably lower cost than originally anticipated. This was because some data, such as from dry deposition samples and local meteorological information, were already being collected on the Toyota site.

1.3.2 The testing program objectives were accomplished, although not much quantitative work was done on the mechanisms of acid rain interaction with wax and paint. Over 2,000 specimens were evaluated after exposure to simulated and real acid rain in the labs at UK and at the Toyota site. Four primary laboratory (or laboratory/field) tests were developed to test the paint/wax specimens under a variety of conditions, in part related to conditions at the Toyota marshalling yard. Those tests were: 1) cyclic evaporation tests (subjecting specimens to different numbers of acid rain evaporation cycles); 2) soaking tests (timed exposure of evaporated acid rain solutions); 3) humidity tests (extended exposure to acid rain solutions under conditions of high humidity); and 4) field exposure tests (extended field exposure of evaporated acid rain solutions). The various exposure and testing conditions are outlined in Sections 3.1, 4.1, 5.1 and 6.1 of this report.

1.4 Terminology

~~1.4.1 Throughout this report the term~~ "waxed" means a specimen was obtained from a larger sample to which the protective wax coating had been applied by Toyota. "Unwaxed" means a specimen never had the protective wax coating applied or that it had been removed by workers at UK. The term "washed" means a specimen was washed after acid rain solution exposure prior to soaking the specimen for a specific time at an elevated temperature. The term "unwashed" means a specimen was not washed between acid rain solution exposure and soaking the specimen for a specific time at an elevated temperature.

2. MONITORING STATION AND Ph TESTING

2.1 Rationale

2.1.1 To effectively characterize the chemistry of precipitation occurring at the Toyota VPI marshalling yard, it was recommended that a wet deposition collector and rain gauge be installed as near as possible to the location of the exposed automobiles (Figure 2.1). This would allow samples to be collected and analyzed for constituents in precipitation: $SO_4^{=}$, NO_3^-,Cl^-, NH_4^+, K^+, Mg^{++}, Ca^{++}, Na^+, and H^+. These data would then be used for two purposes: 1) to determine if there are unusual conditions in the vicinity of the Toyota site which significantly affect the chemistry of precipitation falling there, and 2) to provide actual precipitation samples for use in the laboratory tests.

2.1.2 An additional purpose for installing the monitoring station was to allow Toyota personnel to measure the "dirtiness" of precipitation (as measured by conductivity) immediately after an event occurs. That allows on-site personnel to implement mitigation efforts in a timely fashion after the occurrence of a severe precipitation event.

2.2 Tasks Completed

1. The wet deposition collector and rain gauge were installed at the Toyota VPI marshalling yard on February 23, 1990.

2. Training on the operation of the monitoring equipment was provided to Toyota personnel on February 23 and followed up on February 26.

3. A procedure was adopted whereby a Toyota staff member collected the precipitation sample after each rain event and transported it to the Atmospheric Chemistry Laboratory at the CAER.

4. Each sample was first measured for pH and conductivity and then given a complete chemical analysis if sufficient sample was available. A total of 46 samples were collected from February 23 through August 21, 1990.

5. At the request of Toyota personnel, a method was adopted to notify the marshalling yard personnel of the pH of the most recently collected sample as soon ~~as possible after the sample was received at CAER.~~

6. In discussions with Toyota personnel, it was agreed that an on-site analysis capability was needed at the marshalling yard. A list of needed equipment to accomplish this goal was suggested to Mr. Cecil Ransom on April 24, 1990.

7. In August, the on-site analysis equipment arrived at the Toyota VPI marshalling yard; assistance was provided in the start up of the equipment and training was given in the proper procedures for sample handling.

8. Subsequent to August 21, 1990, Toyota personnel assumed complete operation of the precipitation collection equipment and chemical analysis.

2.3 Results and Discussion

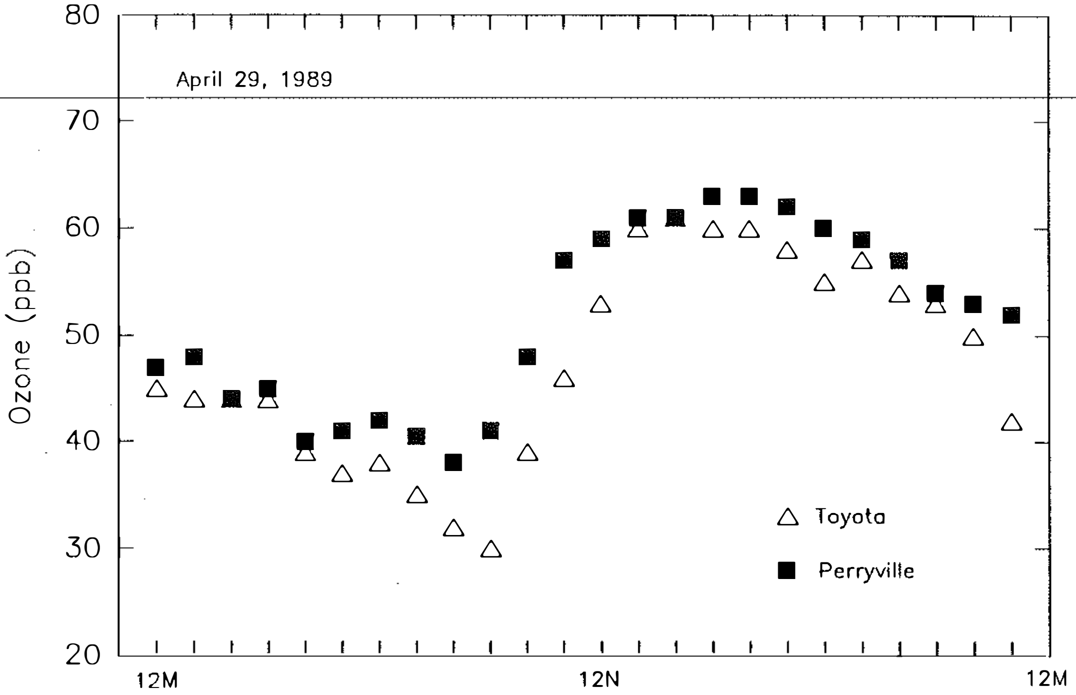
2.3.1 The results obtained for the precipitation samples from the Toyota VPI marshalling yard between February 23 and August 21, 1990 are presented in Table 1. During this time, a total of 46 samples were collected and analyzed. The majority of the collected samples could be classified as "event samples"; i.e., they each represented a single precipitation event. Only one snow sample (No.1) was collected during this time; however, as is typical in the lower Ohio River valley, the pH of this sample was relatively high (5.55).

2.3.2 A comparison of precipitation chemistry data from the Toyota monitoring site with weekly precipitation chemistry data from the Kentucky Acid Deposition Program (KADP) network is presented in Table 2. In this table, Toyota data are compared with both the Lexington monitoring site (located at the University of Kentucky Center for Applied Energy Research, approximately 12 miles from the Toyota site) and with data combined from all nine sites in the KADP network. This comparison indicates that precipitation chemistry occurring at the Toyota VPI marshalling yard is very similar in nature to that of other rural locations in the lower Ohio River valley. The major difference in precipitation composition at Toyota seems to be due to higher dissolved soil and pavement dust (as evidenced by higher conductivity levels and slightly higher Ca^{++} and K^+ concentrations) as well as slightly higher dissolved NH_3 (indicated by higher NH_4^+ concentrations and lower H^+ concentrations). These differences are not surprising due to the monitoring site's proximity to the marshalling yard (hence the soil and pavement dust compounds) and to active agricultural areas (hence the higher NH_3).

2.3.3 As an additional indication of the similarity of the Toyota plant site's immediate atmospheric environment to that of other rural locations in Kentucky, a comparison was made between ground-level O_3 (ozone) concentration data obtained at the Toyota plant site and similar data obtained at the KADP's Perryville Battlefield monitoring site (Figure 2.2). The Perryville site is the only monitoring station in the KADP network having an expanded suite of atmospheric chemical measuring devices including O_3 measurements. Ozone concentrations are the result of a complex set of atmospheric chemical reactions involving nitrogen oxides (NO_x) and various reactive hydrocarbon compounds, and, in essence, give an indication of the reactivity of the local atmosphere. The similarity of the O_3 concentrations for Toyota and Perryville is striking considering that the sites are separated by more than 50 miles.

2.3.4 In summary, a total of 46 precipitation samples were collected at the Toyota VPI marshalling yard and analyzed between February 23 and August 21, 1990. These data provide no evidence that unusual atmospheric conditions exist near the Toyota plant site. Additionally, ozone concentration data obtained both at the Toyota site and at a rural monitoring site in central Kentucky indicate that during the program period the Toyota manufacturing facility did not significantly perturb the local atmospheric chemical environment.

Figure 2.1 Monitoring Station Installed at the Toyota Site.



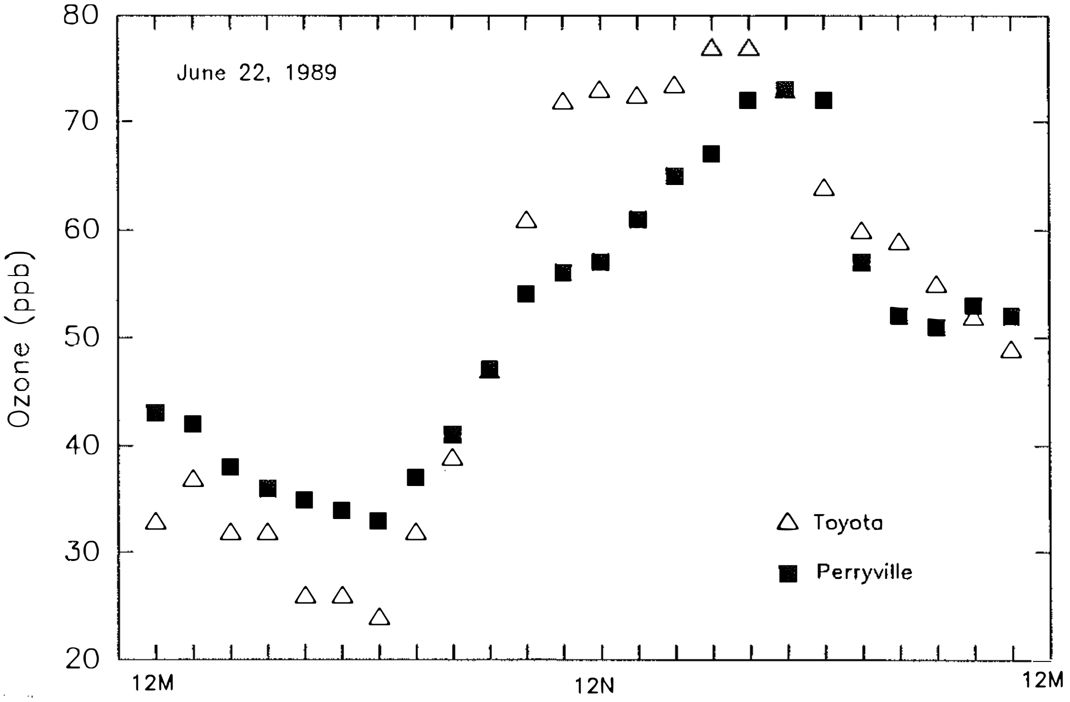


Figure 2.2 Comparison of Ground-Level Ozone Concentrations for the Toyota Plant Site and the Perryville Battlefield Site for April 29 and June 23, 1989.

Table 2.1 Data from the Toyota Precipitation Chemistry Monitoring Station Feb. 23 - Aug. 21, 1990

Sample No.	Date On	Date Off	Precip. depth (mm).	Ph	Conductivity (microS/cm)	(microequivalents/liter)								
						$SO_4^{=}$	NO_3^-	Cl^-	H^+	Na^+	K^+	Ca^{++}	Mg^{++}	NH_4^+
1	2/23	2/26	0.16	5.55	*	*	*	*	2.8	*	*	*	*	*
2	2/26	2/28	0.27	4.13	52.9	71.1	42.7	10.5	74.1	11.4	MDL	31.5	5.6	34.3
3	2/28	3/2	0.92	4.44	31.7	98.9	94.6	16.5	36.3	16.8	2.9	65.4	9.5	37.9
4	3/2	3/9	1.11	4.36	40.6	156.6	84.0	19.0	43.7	21.5	4.4	131.2	11.2	81.4
5	3/9	3/12	3.26	4.61	21.1	64.2	22.1	11.7	24.5	8.3	MDL	26.3	2.6	24.5
6	3/12	3/16	16.36	4.37	26.7	41.6	23.6	4.5	42.7	5.8	MDL	5.1	1.4	22.4
7	3/21	3/23	0.30	4.35	50.7	162.8	91.2	11.7	44.7	21.5	4.1	148.5	20.0	65.8
8	3/23	3/26	3.94	4.19	31.6	36.7	56.2	6.3	64.6	3.3	MDL	11.3	2.1	24.6
9	3/26	3/30	0.16	3.71	156.3	*	*	*	196	*	*	*	*	*
10	3/30	3/30	0.30	4.41	26.5	*	*	*	36.9	*	*	*	*	*
11	3/30	4/3	15.20	4.39	26.8	45.8	24.6	2.3	40.7	2.2	MDL	22.5	5.7	21.2
12	4/3	4/6	0.41	4.04	174.9	448.6	309.0	46.4	91.2	22.5	10.1	*	51.9	306.2
13	4/5	4/10	11.51	4.24	40.8	81.4	36.6	12.0	57.5	12.1	1.4	32.7	3.3	3.0
14	4/10	4/16	14.02	4.31	31.4	55.9	32.4	2.9	49.0	3.8	MDL	5.8	MDL	23.7
15	4/16	5/1	26.04	4.22	40.6	69.6	36.8	11.6	60.3	7.0	0.4	23.3	1.6	26.1
16	5/1	5/2	14.65	4.63	26.8	74.5	26.4	6.1	23.4	4.7	13.6	22.6	2.5	52.5
17	5/2	5/3	1.21	4.16	63.4	168.5	36.7	10.6	66.1	7.4	52.9	44.9	5.8	29.4
18	5/3	5/4	19.83	4.07	56.5	111.4	36.5	5.3	85.1	4.5	0.4	16.5	MDL	35.6
19	5/4	5/7	17.91	4.53	38.9	106.7	44.0	12.6	29.5	16.3	14.9	24.1	14.0	106.9
20	5/7	5/11	1.21	4.50	27.6	56.2	36.7	5.2	31.6	5.6	2.1	36.7	1.8	31.2
21	5/11	5/14	6.14	4.11	44.1	64.2	39.4	6.1	77.6	4.0	1.9	36.3	1.6	24.2
22	5/14	5/16	19.23	4.36	29.0	51.6	26.9	6.1	43.7	6.0	1.7	16.7	MDL	34.3
23	5/16	5/16	26.79	4.80	19.5	38.3	20.5	6.6	25.1	5.2	0.4	9.4	MDL	16.1
24	5/16	5/21	12.31	4.99	9.9	13.5	9.2	7.8	10.2	1.4	0.4	1.4	MDL	9.6
25	5/21	5/23	43.79	4.23	36.2	56.9	26.9	6.7	56.9	1.6	0.4	2.9	MDL	22.6
26	5/23	5/26	0.49	3.62	164.0	*	*	*	240	*	*	*	*	*
27	5/25	5/26	15.61	4.55	22.9	45.4	27.1	8.4	26.2	4.2	0.4	18.0	MDL	17.0
28	5/26	5/29	40.27	4.31	29.2	56.0	14.6	9.9	49.0	3.2	4.3	5.5	1.6	17.6
29	5/29	6/2	13.03	4.46	21.6	46.2	10.9	9.0	33.1	6.0	0.4	5.8	MDL	16.1
30	6/2	6/3	46.36	4.64	12.3	26.4	6.2	10.0	14.5	5.2	0.4	2.6	MDL	13.0

Table 2.1 Data from the Toyota Precipitation Chemistry Monitoring Station Feb. 23 - Aug. 21, 1990
(continued)

31	6/3	6/7	29.10	4.49	20.6	23.9	21.0	9.3	32.4	3.2	0.4	5.6	MDL	11.3
32	6/7	6/14	2.63	3.62	164.1	197.1	105.0	173.0	151	14.0	153.3	102.2	11.0	77.1
33	6/20	6/22	11.09	4.36	26.1	37.3	14.7	6.5	43.7	2.5	0.4	7.7	MDL	26.3
34	6/22	6/24	2.31	4.39	32.3	67.3	31.2	8.0	40.7	4.1	2.0	39.2	5.2	42.6
35	6/24	7/1	0.31	3.95	76.4	*	*	*	112	*	*	*	*	*
36	7/1	7/6	50.65	4.14	38.6	67.7	24.4	6.2	72.4	4.4	0.4	18.8	1.6	19.9
37	7/6	7/13	21.64	4.20	36.0	64.4	36.9	6.0	63.1	4.1	0.4	17.0	3.0	36.6
38	7/17	7/23	17.21	4.20	35.5	77.0	30.5	6.2	63.1	4.7	0.4	9.9	1.3	27.5
39	7/23	7/30	0.49	4.01	294.6	222.1	89.8	476.1	97.7	21.0	511.6	*	*	87.1
40	7/30	8/5	20.02	4.29	36.8	70.3	27.4	9.6	51.3	5.5	1.1	13.2	2.6	26.5
41	8/5	8/6	0.29	3.68	74.0	*	*	*	132	*	*	*	*	*
42	8/6	8/10	2.39	3.71	102.4	213.2	61.1	11.6	196	2.3	0.4	47.3	MDL	31.7
43	8/10	8/13	0.75	3.94	61.9	69.9	36.4	6.6	115	14.5	4.1	28.3	MDL	32.3
44	8/13	8/14	0.91	3.56	125.8	177.3	53.5	5.4	263	5.2	1.2	14.1	MDL	64.3
45	8/14	8/21	0.92	3.64	134.2	338.3	121.3	24.7	229	15.4	10.6	99.1	MDL	98.9
46	8/21	8/21	9.67	4.10	52.5	95.5	38.2	3.9	79.4	7.2	2.4	MDL	MDL	68.01

Legend:

MDL = < minimum detection limit
* = insufficient sample for analysis
# = precipitation depth as measured by rain gauge
+ = specific conductivity measured in microsiemens/cm (micromhos/cm)

Table 2.2 Comparison of Precipitation Chemistry Data from Toyota and the KADP Network

	Avg. pH	PW pH *	Conducttivity ** microS/cm	Precipitation–Weighted Concentrations (microequivalents/liter)								
				$SO_4^{=}$	NO_3^-	Cl^-	H^+	Na^+	K^+	Ca^{++}	Mg^{++}	NH_4^+
Toyota	4.17	4.31	59.3	61.1	26.7	9.5	49.0	5.1	3.1	13.4	1.8	27.1
UKCAER	4.31	4.25	35.1	68.4	26.6	6.7	56.2	5.3	1.2	11.2	2.5	22.7
KADP	4.31	4.28	36.3	57.2	23.4	8.5	52.3	5.5	1.2	9.7	2.9	14.8

Legend:

* = precipitation–weighted pH calculated from PW pH = – $\log[H^+]$

** = specific conductivity measured in microsiemens/cm (micromhos/cm)

3. LABORATORY CYCLIC EVAPORATION TESTING

3.1 Test Objectives and Synopsis

3.1.1 Test Objectives

3.1.1.1 Cyclic evaporation tests were intended to determine whether wetting/evaporation cycles and pH of wetting solutions affected the protective nature of the applied wax and resistance of the paint to damage. Normal exposure of car finishes, both at the Toyota marshalling yard and during typical owner use, involves a series of short exposures to moisture, typically as rain drops, followed by fairly rapid evaporation processes.

3.1.1.2 UK researchers believed that simple exposure to relatively dilute acid concentrations typically encountered in rain and dew might not prove to be sufficiently aggressive to attack the wax/paint by normal wet contact (this was later confirmed by laboratory humidity tests). The acid rain damage would probably result from concentration of acidic compounds during evaporation or possibly by an interaction with sulfur-bearing particles previously deposited on the surface. The latter event was considered less possible.

3.1.1.3 The effect of test temperatures was considered to be a potentially important variable and its effect needed to be factored into the experiments. UK researchers believed that the higher vehicle skin temperatures that promoted rapid evaporation might foster elevated levels of damage. Surface temperature tests at the Toyota marshalling yard indicated the radiant heat from sunlight could result in high skin temperatures on days when the ambient temperature was mild, especially on darker colored vehicles (See Appendix 4). Test temperatures used in laboratory tests were intended to replicate typical vehicle skin temperatures.

3.1.1.4 The degree of wax protection may possibly be related to the damage susceptibility of the paint. If the wax is highly protective, paint damage would only result under what would be considered to be unrealistic service conditions. If the wax was moderately or only slightly protective, damage to the paint would be related to: a) the mitigating effects of the wax coating, b) the severity of the acid attack, and c) the inherent susceptibility of the paint to visually detectable acid rain damage. Therefore, the color (type) of paint employed may also be a contributing factor. UK researchers believed the susceptibility of paint systems employing clear coats to acid rain damage might differ from that of paint systems employing pigmented finish coats. Also, paints of different compositions might have different susceptibilities to acid rain damage. Furthermore, colors might affect visual detectability of paint damage. To account for those possibilities, three different paints representing; light-, intermediate-, and dark-colors were tested (white, light blue, and dark blue, respectively).

3.1.1.5 The acidity of the acid rain solutions employed in the laboratory tests covered a range of pH values from 2.26 to 7.50. This range includes pH values that were considered unlikely to be encountered at the marshalling yard, but which are necessary to characterize the wax/paint performance. Two types of test solutions were employed, those actually obtained from the Toyota marshalling yard monitoring station and those used to simulate acid rain. The simulated acid rain solutions were made at CAER using a formula prescribed by the U.S. Environmental Protection Agency.

3.1.2 Test Synopsis

3.1.2.1 Cyclic evaporation tests involved evaporating a small drop of acid rain from the surface of a small paint/wax-coated specimen representing a vehicle exterior finish. The acid rain wetted specimens were placed in an oven to simulate various ambient temperature conditions encountered at the Toyota marshalling yard during the evaporation process. One evaporation cycle comprised placing a drop of acid rain solution on a wax-coated or unwaxed specimen, placing the sample in the oven, and evaporating the acid rain drop. The specimens were removed from the oven, rinsed, and if necessary, the protective wax was stripped by wiping the test surface with Yuma Industries Inc. **Yumage ST-210** alkaline wax remover. The specimens were then visually inspected for detectable acid rain damage and the results were recorded.

3.2 Test Procedure

3.2.1 Preparation

1. Shear painted/waxed sheet metal furnished by Toyota Motor Manufacturing to form 1-inch square specimens. Protect (painted/waxed) test surface of the sheet metal from surface distress during shearing by covering with paper.

2. Employ a constant-temperature regulated oven. The oven is equipped with an ultraviolet light in a fixture approximately 5 inches from the test surface of the specimens. Set the oven to the test temperature prior to starting a test.

3. Use ambient humidity in test facility during each test.

4. Select the waxed and unwaxed specimens to be used in each test. Typically, specimens (waxed and unwaxed) of one color are employed in a given test. Inspect the test surface to insure the paint/wax is in good condition. Mark the back face of the specimen for identification.

5. Rinse the test surface of each specimen with distilled water.

3.2.2 Testing

1. Deposit one drop of acid rain solution on the test surface of each specimen. The drop has a volume of 0.02 cc. It is measured and deposited from an antiseptic 1-cc syringe (Figure 3.1). The drop is centered on the 1-inch square specimen.

2. Sufficient waxed and unwaxed test specimens of one color are placed on a tray to be tested at one temperature. Each marked specimen is wetted with a drop of the designated acid rain solution. All specimens to be tested are placed on a shallow tray (Figure 3.2). The time between initial wetting and the onset of evaporation of the drops in the oven is limited to the time required to place drops on all test specimens.

3. The tray containing the wetted specimens is placed in the warmed oven (Figure 3.3). During the first test cycle, the specimens are inspected at 5-minute intervals to determine when the drops have evaporated. Once the drops on all the specimens have evaporated, the tray is removed from the oven.

4. Specimens to be tested for one evaporation cycle are removed from the tray for cleaning. Specimens to receive further evaporation cycles are retested as noted in steps 1-3. The operator will remove those specimens from the oven at a time determined from the first test to be suitable for evaporation. This testing procedure will be complete when all the required wetting/evaporation cycles are completed.

3.2.3 Cleaning and Wax Removal

1. The evaporation specimens are rinsed with distilled water.

2. Waxed specimens are stripped with Yuma Industries Inc. **Yumage ST-210** wax remover. Those specimens are immersed in a petri dish filled with the wax remover for 2 minutes. Then, they are rinsed with distilled water.

3. The specimens are placed singly in petri dishes filled with distilled water. They are ultrasonically cleaned for 5 minutes, rinsed with distilled water, and air dried.

3.2.4 Inspection

1. The specimens of each test series (test type, test temperature, and color) are mounted on a display board (Figure 3.4). The board indicates the number of test cycles and test pH for each specimen.

2. The specimens are visually inspected independently by two researchers. The specimens are inspected indoors under ultraviolet light. The researchers record whether or not they see visible damage to the surface of the specimens on test sheets.

3. The two researchers compare their test sheets and re-inspect the specimens. If the researchers agree on the condition of the specimens, the final records will indicate ND (not damaged) or D (damaged). If they disagree, the condition for a particular specimen will be recorded as PD (possible damage).

3.3 Test Parameters and Conditions

3.3.1 Test Parameters

3.3.1.1 The test matrix for this process covered 1, 3, 6, 9, and 12 evaporation cycles, three oven temperatures (110, 150, and 170 °F), three colors (white, light blue, and dark blue), specimens which were waxed or unwaxed, and 11 acid rain pH values. Nine of the pH solutions were made in a laboratory according to EPA guidelines (pH values of 2.26, 2.50, 3.20, 3.70, 5.00, 6.00, 6.80, 7.20, and 7.50). The other two solutions (pH values of 4.40 and 4.60) were collected at the Toyota plant. These values are listed on the test data sheets in this report. During the cyclic evaporation tests, 538 specimens were tested. Not all specimen types (in terms of color and wax condition) and test conditions (in terms of evaporation temperature and pH solutions) were employed during this series of tests. The extent of testing was limited by specimen availability and procurement of additional synthesized and natural acid rain solutions. Evaporation tests were not performed on dark blue specimens at 150 °F.

3.3.2 Test Conditions

3.3.2.1 The variability of the acid rain droplet deposition was ± 0.005 cc. The ambient test temperature varied between 70 to 80 °F. The relative humidity was not controlled. However, at each of the selected test temperatures, the evaporation times did not vary by more than 5 minutes. The oven, a General Signal **BLUE M STABIL-THERM** batch oven, operated on an intermittent feedback temperature control. During the tests, the oven temperature was observed to vary by 7 °F. The effect of sunlight was compensated for by placing a Phillips Lighting **Colortone 50** fluorescent lamp in the oven during all heating tests. That type of lamp closely duplicates the spectral characteristics of natural daylight at a color temperature of 5,000 °K. The lamp provided approximately 2,000 lux illumination in the oven. The two researchers inspecting the test specimens were capable of reading a Jaeger 1 eye chart at arm's length. Inspections were conducted indoors under neon light (1,400 lux incident light) without use of visual aids such as magnifiers.

3.4 Profilometry, Optical Microscopy, SEM, and EDX

3.4.1 Profilometry

3.4.1.1 All samples subjected to cyclic evaporation tests were analyzed by profilometry to measure the thickness of the wax coatings on specimens and also the depth of surface damage. The profilometer used was an in-house machine consisting of a motor-driven sample stage and a stationary stylus. The samples were mounted on a magnetic sample holder on the stage (Figure 3.5). The sensitivity of measurement could be varied to desired levels (as low as 0.01 microns) by interfacing the output from the profilometer to an Instron machine. The stylus was manually positioned to start from one edge of the damaged/wax-removed sample. As the sample moved, measurements were recorded for a maximum distance of about 4 cm.

3.4.1.2 To measure the thickness of coatings, a narrow strip of wax on a specimen was removed using the wax remover. Portions of the specimen on either side of the stripped area retained the wax. Those areas served as a datum over which the profilometer stylus travelled. The stylus deflected downward when it encountered the stripped area and rebounded when it passed across the adjacent wax-coated areas. The difference in height readings between the datum (waxed areas) and the stripped area was the wax coating thickness. For the cyclic evaporation tests, the wax coating thicknesses on the white specimens varied from 1.8 to 10.5 microns; on the light blue specimens from 2.6 to 8.0 microns; and on the dark blue specimens from 2.7 to 6.6 microns.

3.4.1.3 The profilometer was also used to measure the depth of acid rain damage in relation to the top surface of the waxed specimens. Those tests indicated shallow surface damage in the wax. For the 110 °F tests of light blue specimens, the depth of that damage in the wax coating was about 3 microns for acid rain tests with Ph values above 3.0 (See Figure 3.6). Below that Ph value, the depth of damage penetration increased until it exceeded the thickness of the wax coating.

3.4.2 Optical Microscopy

3.4.2.1 Specimens damaged by evaporation of acid rain solutions were inspected using an optical microscope at magnifications of 50X. Typically, undamaged paint surfaces were relatively flat with random scratches that probably occurred during handling. The inspections revealed what appeared to be etching damage and crazing at locations where disturbances could be detected with unaided vision.

3.4.2.2 Initially, UK researchers intended to perform inspections using optical microscopes, but switched to visual inspections. Though optical microscopes were better indicators of the actual presence of damage than unaided visual inspections, the latter provided a level of acceptable damage. UK researchers felt that was needed to judge when "unacceptable" damage occurred. Subsequent inspections were employed using a scanning electron microscope to overcome depth-of-field problems in examining typical acid rain damage.

3.4.3 SEM and EDX Testing

3.4.3.1 SEM inspections were performed on uncleaned damaged specimens (Figure 3.7). In an effort to identify the chemical elements present in the damaged area, SEM/EDX analysis was carried out on select test specimens. This was achieved by using an ultra-thin window detector capable of detecting light elements (such as Boron) attached to a state-of-art computer workstation. The characteristic X-rays emitted from the sample surface due to bombardment by the electron beam were collected and the relative intensity/position was used to identify the elements. An EDX scan of the damaged specimen shown in Figure 3.8 revealed the presence of the elements C, N, O, Cu, Zn, Si, P, S, and Cl (Figure 3.8). Sulfur was not present in similar untested specimens and was probably provided by the acid rain solution.

3.5 Test Results

3.5.1 Visual Inspections

3.5.1.1 After the evaporation tests were performed, visible crustaceous deposits were present on the surface of the test specimens (Figure 3.9). Those deposits were commonly circular shaped and were present in the center of the specimens where the acid rain solutions had been deposited prior to evaporation tests. Those deposits were heavier for both the artificial acid rain solutions and in most cases for the more acidic solutions. During the cleaning process most crustaceous deposits were removed. When visible damage was present, it commonly appeared as a ring or set of concentric rings at the previous periphery of the crustaceous deposits. Typically, the paint surface enclosed by the rings would remain relatively undamaged (See Figure 3.7). Inspections of that damage showed it to be typically etching of the paint. The detectable presence of etching served as the criterion to determine whether the paint had been damaged [i.e. the wax had not (or had) protected the paint].

3.5.1.2 The inspectors did not have difficulties in assessing damage to specimens exposed to low Ph acid rain solutions (3.20 or less). In most cases, that damage was very severe and obvious. Damage at higher Ph values was less apparent and harder to discern. The light blue (metallic blue) specimens were the most difficult to assess. Patterns in the pigmented base coat of the paint replicated some damage patterns and made damage inspection difficult.

3.5.2 Wax Coating/Paint Performance

3.5.2.1 The results from the cyclic evaporation tests are listed in Tables 3.1 to 3.8. In every test, damage was produced on both waxed and uncoated specimens by some acid rain solutions (real or artificial). Typically, tests at Ph values less than 3.0 tended to produce damage regardless of test temperatures, number of cycles, or color (with the exception of light blue specimens tested at 170 °F). For all cyclic evaporation tests, 76 percent of the specimens tested with Ph values less than 3.20 were damaged. Damage to specimens exposed to higher Ph acid rain solutions was less common (10 percent).

3.5.2.2 Trends for cyclic evaporation test data were discerned by the quantitative analyses presented in Appendix 2, Figures 2-8. There was a trend toward greater damage to both waxed and unwaxed specimens exposed to lower Ph solutions. Also, there was a trend toward greater damage with more evaporation cycles for both waxed and unwaxed specimens. The test data indicated an increased level of protection for waxed specimens compared to the unwaxed specimens at all levels of acid rain exposure based on either Ph values or number of exposure cycles. Correlations of damage vs Ph for various test temperatures did not reveal a clear relationship between test temperature and damage. The dark blue paint was less susceptible to damage at low evaporation cycles than the white or light blue paints. However, that difference decreased at higher evaporation cycles. The wax provided a measure of increased protection for all three test colors.

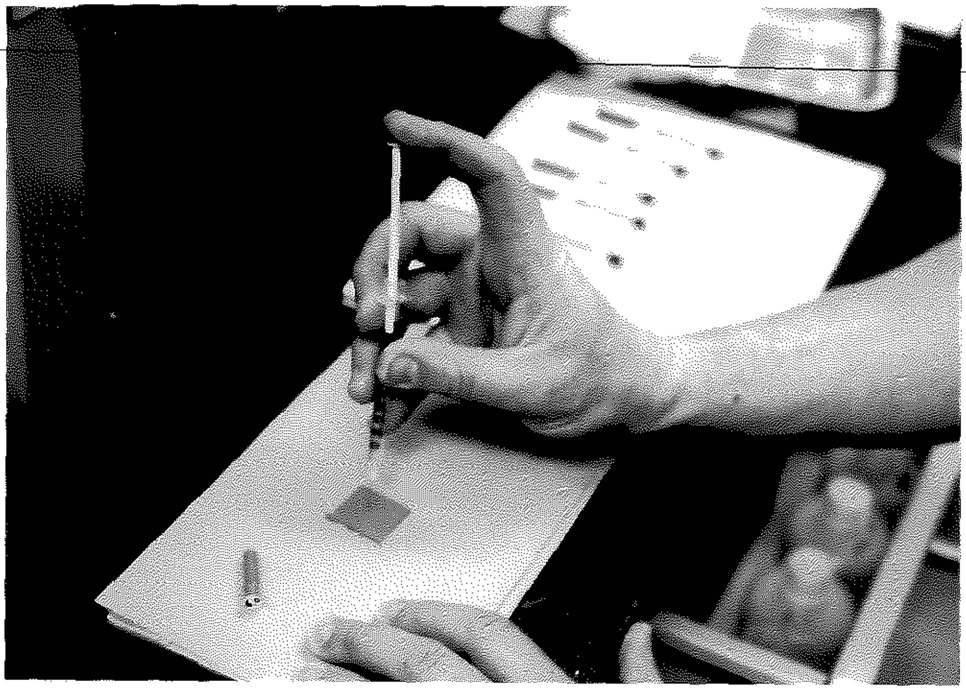


Figure 3.1 Application of Acid Rain Solution to a Test Specimen Using a Syringe.

Figure 3.2 Wetted Specimens on a Tray Prior to Insertion in the Oven for Evaporation Tests.

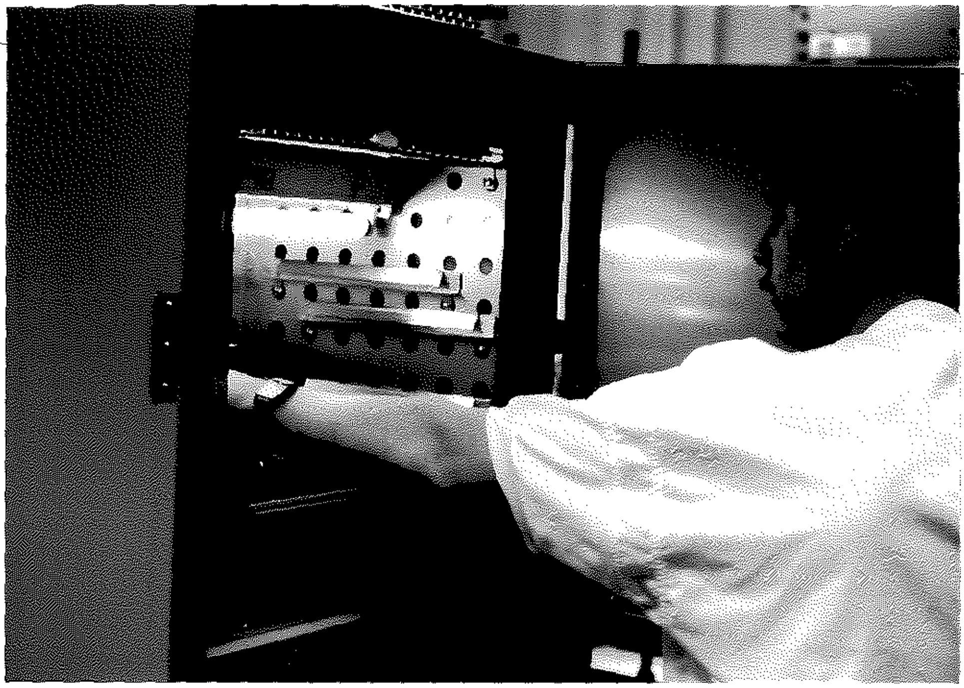


Figure 3.3 Technician Inserting a Tray of Evaporation Test Specimens into the Oven. Note the Ultraviolet Lamp in the Oven.

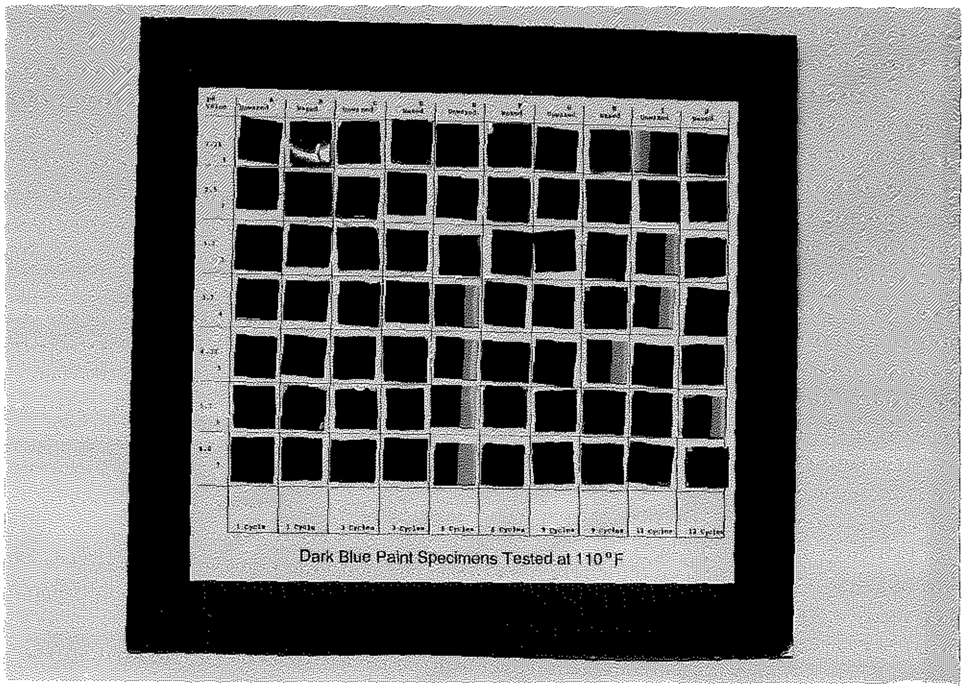


Figure 3.4 Specimens Mounted on a Display Board for Inspection.

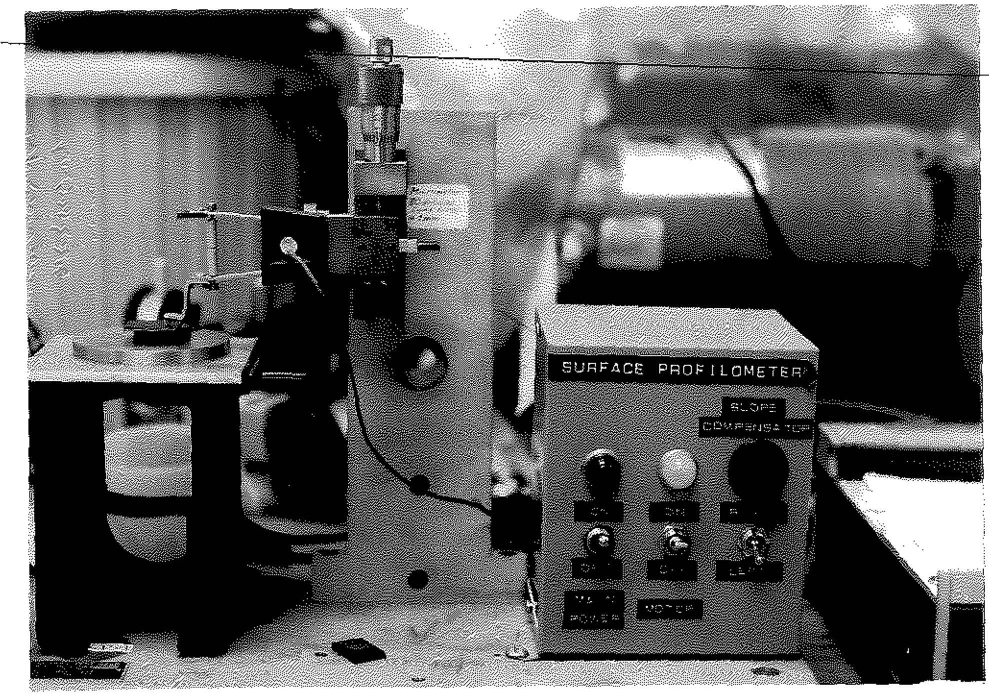


Figure 3.5 Profilometer Used to Measure Coating Thickness and Depth of Acid Rain Damage.

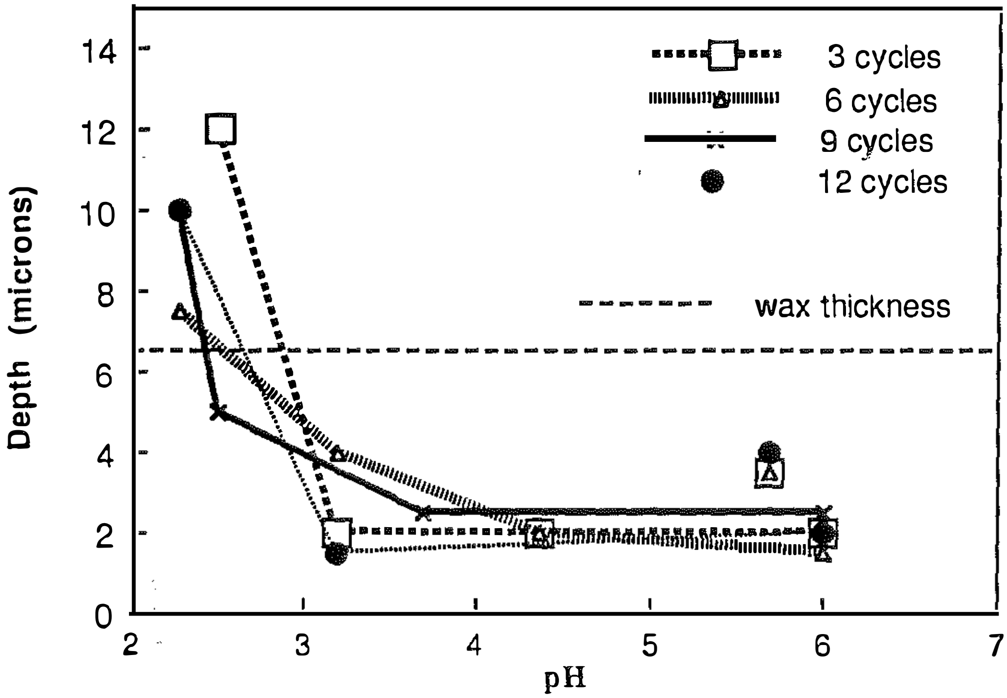


Figure 3.6 Profilometry Measurement of Depth of Damage Penetration vs Acid Rain Solution pH for Cyclic Evaporation Tests of Light Blue Specimens at 110 °F.

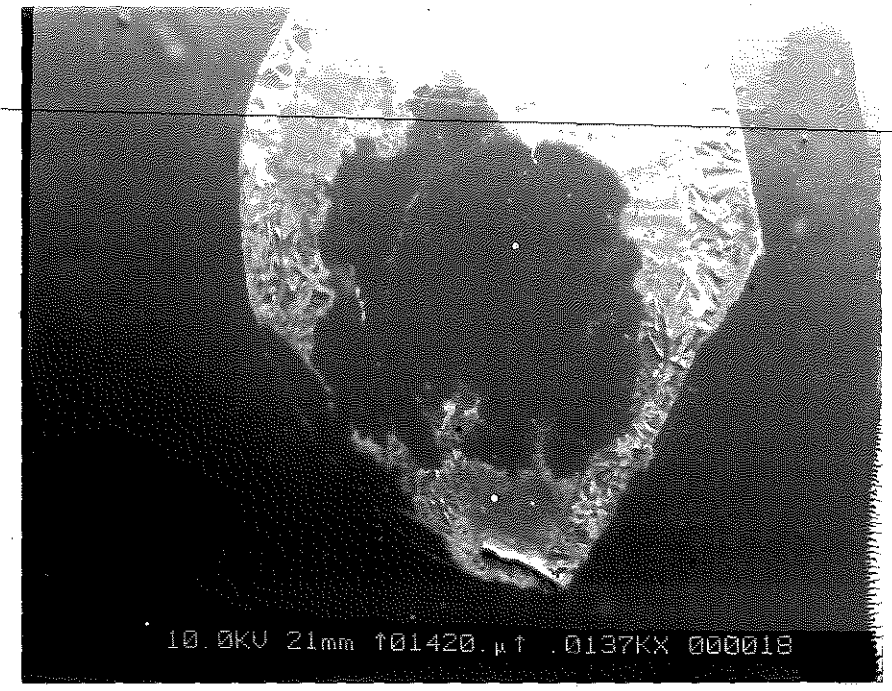


Figure 3.7 SEM Photograph of a Dark Blue Unwaxed Sample Exposed to a 3.2 pH Solution. (Note the Relatively Undamaged Surface Area Surrounded by Etching Damage).

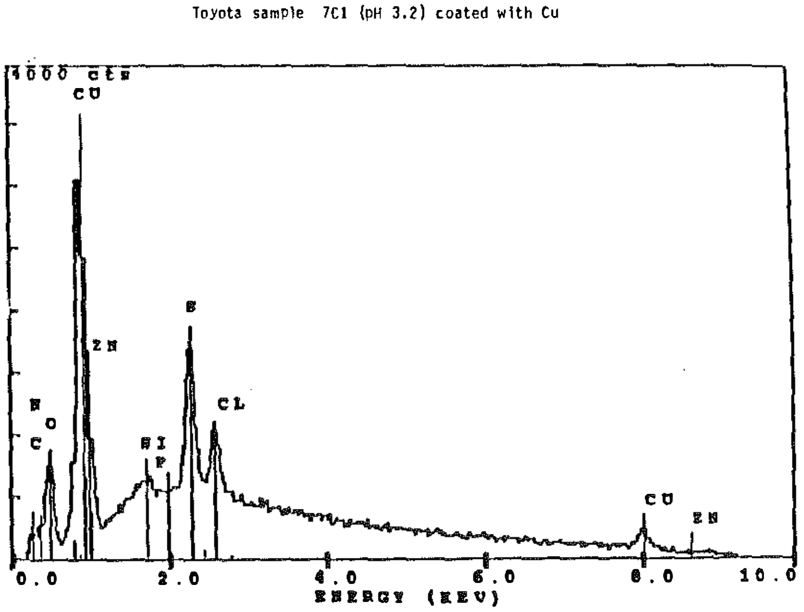


Figure 3.8 EDX Scan of Damaged Unwaxed Specimen Shown in Figure 3.5. Elements Identified - C, N, O, Cu, Zn, Si, P, S, and Cl.

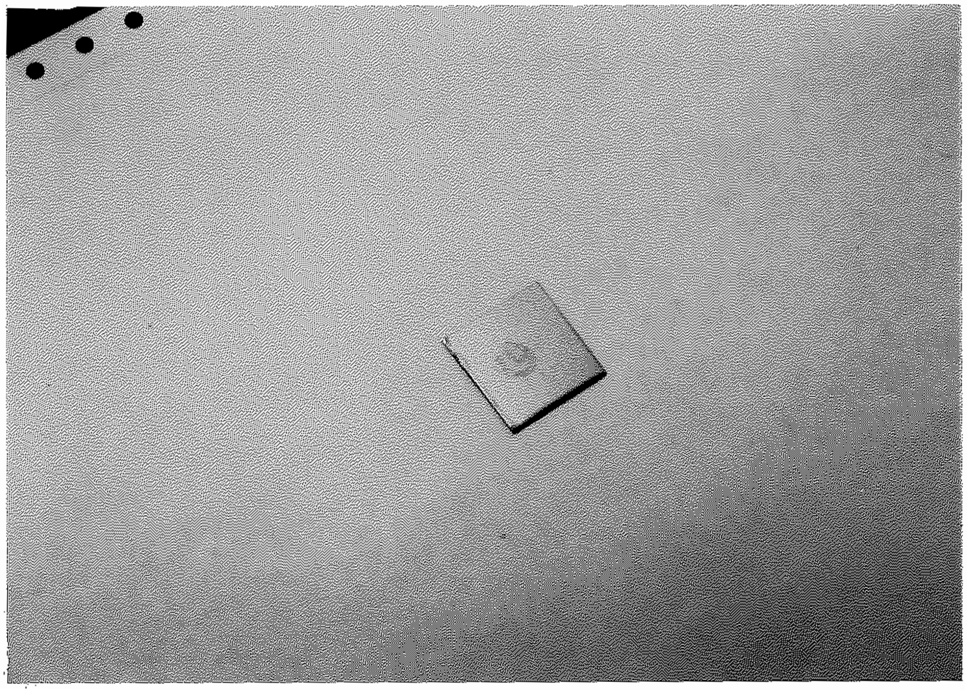


Figure 3.9 A Typical Crustaceous Deposit on the Surface of a Test Specimen after Evaporation Testing. A Light Blue Specimen Is Shown.

Table 3.1 CYCLIC EVAPORATION TESTS FOR WHITE SPECIMENS TESTED AT 110 °F

	NUMBER OF EVAPORATION CYCLES									
pH	1		3		6		9		12	
	UW	W	UW	W	UW	W	UW	W	UW	W
2.26	D	D	D	D	D	D	D	D	D	D
2.50	D	D	D	D	D	D	D	D	D	X
3.20	D	PD	D	D	D	D	D	D	D	X
3.70	ND	ND	ND	ND	ND	ND	PD	ND	ND	X
5.00	ND	ND	ND	ND	ND	ND	ND	ND	ND	X
7.20	ND	ND	ND	ND	PD	ND	PD	ND	PD	X
7.50	ND	ND	ND	ND	ND	ND	ND	ND	ND	X

Legend:
UW - Unwaxed specimen.

W - Wax coated specimen.

X - No specimen tested.

ND - No visible damage to specimen.

PD - Possible damage to specimen (inspectors disagree).

D - Visible damage to specimen.

Note: For these tests, the wax coating thickness ranged from 6.5 to 10.5 m based on 76 specimen measurements.

Table 3.2 CYCLIC EVAPORATION TESTS FOR WHITE SPECIMENS TESTED AT 150°F

pH	NUMBER OF EVAPORATION CYCLES									
	1		3		6		9		12	
	UW	W	UW	W	UW	W	UW	W	UW	W
2.26	D	X	D	D	D	X	D	X	D	D
2.50	D	X	D	D	D	X	D	X	D	D
3.20	D	X	D	PD	D	X	D	X	D	D
3.70	ND	X	ND	ND	ND	X	ND	X	D	ND
5.00	ND	X	ND	ND	ND	X	ND	X	ND	ND
7.20	ND	X	ND	ND	ND	X	ND	X	ND	X
7.50	ND	X	ND	ND	ND	X	ND	X	ND	X

Legend: UW - Unwaxed specimen.

W - Wax coated specimen.

X - No specimen tested.

ND - No visible damage to specimen.

PD - Possible damage to specimen (inspectors disagree).

D - Visible damage to specimen.

Note: For these tests, the wax coating thickness ranged from 9.0 to 10.5 microns based on 46 specimen measurements.

Table 3.3 CYCLIC EVAPORATION TESTS FOR WHITE SPECIMENS TESTED AT 170°F

pH	NUMBER OF EVAPORATION CYCLES									
	1		3		6		9		12	
	UW	W	UW	W	UW	W	UW	W	UW	W
2.26	D	D	D	D	D	D	D	D	D	D
2.50	D	D	D	D	D	D	D	D	D	D
3.20	D	ND	D	PD	D	D	D	D	D	D
3.70	ND	ND	PD	ND	D	ND	D	PD	D	PD
(4.40)	ND	ND	PD	ND	PD	ND	ND	ND	ND	ND
(4.60)	ND	ND	ND	ND	D	ND	PD	ND	ND	PD
5.00	ND	ND	PD	ND	D	ND	PD	ND	D	ND
6.00	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
6.80	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
7.20	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
7.50	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

Legend: ( ) - Actual rain sample from Toyota plant.

UW - Unwaxed specimen.

W - Wax coated specimen.

X - No specimen tested.

ND - No visible damage to paint.

PD - Possible damage to paint (inspectors disagree).

D - Visible damage to paint.

Note: For these tests, the wax coating thickness ranged from 1.8 to 2.6 microns based on 5 specimen measurements.

Table 3.4 CYCLIC EXPOSURE TESTS FOR LIGHT BLUE SPECIMENS TESTED AT 110 ^{o}F

	NUMBER OF EVAPORATION CYCLES									
	1		3		6		9		12	
pH	UW	W	UW	W	UW	W	UW	W	UW	W
2.26	D	D	D	D	D	D	D	D	D	D
2.50	X	X	D	D	D	D	D	D	D	X
3.20	PD	X	PD	D	PD	D	D	D	D	X
3.70	D	X	PD	ND	D	ND	PD	ND	PD	PD
5.00	X	X	PD	PD	PD	PD	D	ND	PD	PD
7.20	ND	X	ND	ND	D	ND	PD	ND	ND	ND
7.50	ND	X	ND	ND	D	PD	ND	ND	ND	ND

Legend: UW - Unwaxed specimen.

W - Wax coated specimen.

X - No specimen tested.

ND - No visible damage to paint.

PD - Possible damage to paint (inspectors disagree).

D - Visible damage to paint.

Note: For these tests, the wax coating thickness ranged from 5.5 to 7.0 m based on 22 specimen measurements.

Table 3.5 CYCLIC EXPOSURE TESTS FOR LIGHT BLUE SPECIMENS TESTED AT 150°F

	NUMBER OF EVAPORATION CYCLES									
pH	1		3		6		9		12	
	UW	W	UW	W	UW	W	UW	W	UW	W
2.26	D	X	D	X	D	X	D	X	D	X
2.50	D	D	D	X	D	X	D	X	X	X
3.20	X	PD	ND	X	D	X	D	X	X	X
3.70	ND	ND	ND	X	PD	ND	PD	ND	X	X
5.00	X	ND	ND	X	ND	ND	PD	ND	X	X
7.20	PD	ND	X	X	X	X	ND	X	ND	ND
7.50	ND	ND	X	X	ND	X	ND	X	ND	ND

Legend: UW - Unwaxed specimen.

W - Wax coated specimen.

X - No specimen tested.

ND - No visible damage to specimen.

PD - Possible damage to specimen (inspectors disagree).

D - Visible damage to specimen.

Note: For these tests, the wax coating thickness ranged from 6.0 to 8.0 microns based on 36 specimen measurements.

Table 3.6 CYCLIC EVAPORATION TESTS FOR LIGHT BLUE SPECIMENS TESTED AT 170°F

pH	NUMBER OF EVAPORATION CYCLES									
	1		3		6		9		12	
	UW	W	UW	W	UW	W	UW	W	UW	W
2.26	PD	PD	D	ND	D	PD	D	ND	D	PD
2.50	D	ND	D	ND	D	ND	D	ND	D	ND
3.20	ND	ND	D	ND	D	ND	D	ND	D	ND
3.70	ND	ND	ND	X	PD	ND	PD	ND	PD	ND
(4.40)	D	ND	D	ND	D	ND	D	ND	D	ND
(4.60)	PD	ND	D	ND	D	ND	D	ND	D	ND
5.00	D	ND	D	ND	D	ND	PD	D	D	ND
6.00	PD	ND	PD	ND	D	PD	D	ND	D	ND
6.80	ND	X	ND	X	ND	PD	ND	X	ND	X
7.20	PD	ND	ND	ND	ND	ND	ND	D	PD	ND
7.50	ND	ND	ND	ND	ND	ND	PD	ND	PD	ND

Legend:	
( )	Actual rain sample from Toyota plant.
UW	Unwaxed specimen.
W	Wax coated specimen.
X	No specimen tested.
ND	No visible damage to paint.
PD	Possible damage to paint (inspectors disagree).
D	Visible damage to paint.

Note: For these tests, the wax coating thickness ranged from 2.7 to 4.0 m based on 5 specimen measurements.

Table 3.7 CYCLIC EVAPORATION TESTS FOR DARK BLUE SPECIMENS TESTED AT 110 °F

pH	NUMBER OF EVAPORATION CYCLES									
	1		3		6		9		12	
	UW	W	UW	W	UW	W	UW	W	UW	W
2.26	D	X	D	D	D	D	D	D	D	D
2.50	D	D	D	D	D	X	D	D	D	D
3.20	D	PD	D	PD	D	D	D	D	D	D
3.70	ND	ND	ND	ND	ND	ND	ND	ND	PD	PD
5.00	ND	ND	PD	ND	ND	PD	ND	D	D	ND
6.80	PD	ND	ND	ND	D	ND	PD	ND	PD	ND
7.50	PD	ND	ND	ND	PD	ND	ND	ND	ND	ND

Legend: UW - Unwaxed specimen.

W - Wax coated specimen.

X - No specimen tested.

ND - No visible damage to paint.

PD - Possible damage to paint (inspectors disagree).

D - Visible damage to paint.

Note: For these tests, the wax coating thickness ranged from 5.8 to 6.6 microns based on 2 specimen measurements.

Table 3.8 CYCLIC EVAPORATION TESTS FOR DARK BLUE SPECIMENS TESTED AT 170°F

pH	NUMBER OF EVAPORATION CYCLES									
	1		3		6		9		12	
	UW	W	UW	W	UW	W	UW	W	UW	W
2.26	D	ND	D	ND	PD	PD	PD	PD	PD	D
2.50	ND	D	ND	X	PD	X	PD	X	D	X
3.20	ND	ND	ND	PD	PD	PD	PD	D	PD	PD
3.70	ND	ND	ND	PD	PD	PD	PD	D	PD	PD
(4.40)	ND	ND	ND	ND	ND	ND	ND	ND	PD	ND
(4.60)	ND	ND	ND	ND	ND	ND	ND	ND	D	ND
4.80	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
5.00	ND	ND	ND	ND	ND	ND	PD	ND	D	ND
6.80	ND	ND	ND	ND	ND	ND	ND	ND	D	ND
7.20	ND	ND	ND	ND	ND	ND	ND	ND	D	PD
7.50	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

Legend: ( ) - Actual rain sample from Toyota plant.

UW - Unwaxed specimen.

W - Wax coated specimen.

X - No specimen tested.

ND - No visible damage to paint.

PD - Possible damage to paint (inspectors disagree).

D - Visible damage to paint.

Note: For these tests, the wax coating thickness ranged from 2.7 to 4.0 microns based on 5 specimen measurements.

4. LABORATORY SOAK TESTS

4.1 Test Objectives and Synopsis

4.1.1 Test Objectives

4.1.1.1 Laboratory soak (timed exposure) tests were performed to determine the wax protection in relation to acid rain deposition followed by long-term exposure at elevated temperatures. Aspects of the tests were based on a test procedure formulated by Toyota personnel which they used as an acceptance test for evaluating the suitability of wax coatings. The soaking duration (elevated temperature exposure) was based on periods of high temperatures experienced by the vehicles during storage. At the time of that set of experiments, it was anticipated that the vehicles were to be exposed for periods up to four weeks. UK researchers felt that the vehicles would experience the maximum temperature for about 12 hours per day. Therefore, a maximum period of thermal exposure of 336 hours (two weeks) was chosen. The test temperatures chosen were typical of storage temperatures encountered at the Toyota marshalling yard. Temperatures of 110, 150, and 170 °F were selected to represent the maximum (daytime) exposure temperatures encountered at the marshalling yard. In part, those temperatures were based on surface temperature measurements taken at the marshalling yard (See Appendix 4). Specimens of the three basic test colors: dark blue, white, and light blue were tested.

4.1.1.2 The laboratory soak tests were also employed to investigate the protective effect of washing the stored vehicles after an acid rain exposure. In practice, VPI washed the vehicles within 24 hours of an acid rain event having a pH less than 4.0. For the laboratory soak tests, the effect of washing was investigated for acid rain solutions having pH values up to 7.5. Most of the acid rain solutions were used in the other series of laboratory and laboratory/field tests. To determine the extent of protection provided, the acid-rain exposure was limited to one evaporation cycle and tests were performed in both the washed and unwashed conditions.

4.1.1.3 The specimens employed in laboratory soak tests differed from the specimens employed in the initial cyclic evaporation tests. The specimens used in the laboratory soak tests employed aftermarket paint and were coated using the production line wax application spray system at Toyota Motor Manufacturing. The coatings were thinner than those used in the cyclic evaporation tests and varied between 4.3 to 6.3 microns.

4.1.2 Test Synopsis

4.1.2.1 Soak tests involved evaporating a drop of acid rain from the surface of a small wax coated painted specimen representing a vehicle exterior surface. The drops were evaporated in an oven. Two sets of specimens were tested; one set was washed after the evaporation process, and the other set was left untreated. Specimens were placed in the oven to simulate storage at typical daytime temperatures. After soaking different groups of specimens at different times and soak temperatures, they were removed from the oven, rinsed, and the protective wax coating was stripped off. The specimens were visually inspected for acid rain damage and the results were subsequently recorded.

4.2 Test Procedure

4.2.1 Preparation

1. Shear painted/waxed sheet metal furnished by Toyota Motor Manufacturing to form 1-inch square specimens. Protect the sheet metal from surface distress during shearing by covering with paper.

2. Employ constant temperature regulated oven. The oven is equipped with an ultraviolet light in a fixture approximately 5 inches from the test surface of the specimens. Set the oven to the selected temperature prior to starting a test.

3. Use ambient humidity in test facility during each test.

4. Select waxed specimens to be used for this test. Inspect the test surface to insure the paint/wax is in good condition. Mark the back face of the specimens for identification.

5. Divide the test surface into four sections with an oil-based marker.

6. Rinse the test surface of each specimen with distilled water.

4.2.2 Testing

1. Deposit four drops of different pH values of acid rain solution on the test surface of each specimen. Each drop has a volume of 0.02 cc. It is measured and deposited from an 1-cc syringe. The drops are centered in each of the four sections of a 1-inch square specimen.

2. Sufficient test specimens of each color are placed on a tray to be tested at the selected temperature. These waxed specimens are divided into three categories: control group, washed, and unwashed. Each marked specimen is wetted with drops of the designated acid rain solutions. The time between initial wetting and evaporation of the drops in the oven is limited to the time required to place drops on all the specimens to be tested.

3. The specimens are placed in the warmed oven. They are inspected at 5-minute intervals to determine when the drops have evaporated. Once the drops have evaporated on all of the specimens, the tray is removed from the oven.

4. The control group specimens are removed from the tray, rinsed with tap water, and allowed to air dry. That group is separated from the other specimens and set aside for cleaning, wax removal, and subsequent inspection. The washed group is rinsed with tap water, put back on the tray along with the companion set of unwashed specimens, and returned to the oven to soak for the specified time.

5. The washed and unwashed specimens will soak in the oven for multiple 1-day periods. These soak periods vary from 1 to 14 days. When they have been soaked for the specified duration, the specimens will be removed, cleaned, stripped of wax, and inspected. The test will end when the 14-day soak tests are completed.

4.2.3 Cleaning and Wax Removal

1. The wax is stripped with Yuma Industries **Yumage ST-210** wax remover. The specimens are immersed in a petri dish filled with the wax remover for 2 minutes. Then, they are rinsed with distilled water.

2. The specimens are placed singly in petri dishes filled with distilled water. They are ultrasonically cleaned for 5 minutes, rinsed with distilled water, and air-dried.

4.2.4 Inspection

1. All specimens tested at one temperature are mounted on a display board. Specimen locations are determined by pH value, soaking period, and group (control, washed, or unwashed).

2. The specimens are visually inspected independently by two researchers. They are inspected indoors under ultraviolet light. The researchers record whether they detect visible damage to the surface of the specimens.

3. The researchers compare their inspection results and re-inspect the specimens. If the researchers agree on the condition of the specimens, the final records will indicate ND (not damaged) or D (damaged). If the inspectors do not agree, the condition for a particular specimen will be recorded as PD (possible damage).

4.3 Test Parameters and Conditions

4.3.1 Test Parameters

4.3.1.1 The test matrix for this process included control specimens (exposed to one cycle of acid rain evaporation, but no soaking), soaking periods of 24, 72, 120, 168, and 336 hours, three oven temperatures (110, 150, and 170 °F), three colors (white, light blue, and dark blue), specimens which were waxed and washed or unwashed after the acid rain solution evaporation exposure, and 12 acid rain solutions of different pH values. Eight of the pH solutions were made in a laboratory according to EPA guidelines (pH values of 2.25, 2.50, 3.20, 3.70, 5.00, 6.00, 6.80, and 7.50). The other four solutions (pH values of 3.58, 3.71, 4.40, and 4.60) were collected at the Toyota plant. During the soak tests, 1,179 specimens were tested. All specimen types (in terms of color and wax condition) and test conditions (in terms of soak times, temperature and pH solutions) were employed during this series of tests.

4.4 Profilometry

4.41 The wax coating thicknesses on the specimens were measured using the profilometry technique described in 3.4.1.2. The wax coating thickness varied from 5.8 to 6.1 microns for dark blue specimens, 6.0 to 6.1 microns for white specimens, and 4.3 to 6.3 microns for light blue specimens.

4.5 Test Results

4.5.1 Visual Inspections

4.5.1.1 After the initial evaporation of the acid rain solution, surface deposits were observed on the wax-coated surfaces of many specimens. The washing procedure used for the "washed" specimens prior to soaking did not eliminate those deposits. On completion of the soak tests, damage detected after cleaning and stripping the wax was observed at previous sites of surface deposits.

4.5.2 Wax Coating/Paint Performance

4.5.2.1 The control test results are presented in Tables 4.1 to 4.18. The control test results show a slight increase in damage between 110 and 170 °F. Most damage to the control (no-soak) specimens occurred at or below pH values of 3.20 (78 percent) compared to control specimens tested at higher pH exposures (1 percent). Soaking increased the incidence of damage for the tests at pH exposures above 3.20, but only to a small degree. The 110 °F soak tests had 67 percent damage for specimens tested at pH values below 3.20, but no specimens tested with pH values above 3.20 were damaged. The 150 °F soak tests had an 84 percent damage rate for specimens tested at pH values below 3.20, but 3 percent damage for specimens tested at higher pH values. The 170 °F soak tests had 97 percent damage to specimens tested at pH values below 3.20 compared to 8 percent for specimens tested at higher pH values.

4.5.2.2 Trends for soak test data were discerned by quantitative analyses presented in Appendix 2, Figures 9-25. There was a trend toward greater damage to both washed and unwashed specimens exposed to lower pH solutions. The unwashed specimens had a slightly higher trend for damage than the washed specimens throughout the range of pH values and soak times tested. Soak time did not appear to be a determining factor. Washing had a beneficial (damage-reducing) effect on all three paint colors throughout the range of pH values tested. Considering all soak tests, the difference in amount of damage between the washed and the unwashed specimens soak tested at 150 and 170 °F was much greater than the specimens tested at 110 °F. However, for the data of each of the three colors, soak temperature did not have a consistent effect on damage Generally, the effect of soak test temperature tends to decrease at lower test pH values. For the washed specimens, the light blue specimens were slightly more prone to damage throughout the range of pH values for the soak tests.

TABLE 4.1 CONTROL RESULTS, 110 °F SOAK TESTS			
pH	**D BLUE**	**WHITE**	**L BLUE**
2.26	D	D	D
2.50	D	D	ND
3.20	ND	ND	ND
(3.58)	ND	ND	ND
3.70	ND	ND	ND
(3.71)	ND	ND	PD
(4.40)	ND	ND	ND
(4.60)	ND	ND	ND
5.00	ND	ND	ND
6.00	ND	ND	ND
6.80	ND	ND	ND
7.50	ND	ND	ND

Legend: ( ) - Actual rain sample from Toyota plant.

D - Detectable damage to paint.

PD - Possible damage to paint (inspectors disagree).

ND - No detectable damage to paint.

Note: The wax coating thicknesses (from two tests for each paint color):

Dark Blue - 5.8 to 6.1 microns

White - 6.0 to 6.1 microns

Light Blue - 4.3 to 6.3 microns

TABLE 4.2 24-HOUR SOAKING TEST (110 °F)

pH	(WASHED)			(UNWASHED)		
	D BLUE	WHITE	L BLUE	D BLUE	WHITE	L BLUE
2.26	D	D	D	D	D	D
2.50	D	ND	D	D	D	D
3.20	ND	ND	PD	ND	ND	PD
(3.58)	ND	ND	ND	PD	ND	ND
3.70	ND	ND	ND	ND	ND	ND
(3.71)	ND	ND	ND	ND	ND	ND
(4.40)	ND	ND	ND	ND	ND	ND
(4.60)	ND	ND	ND	ND	ND	ND
5.00	ND	ND	ND	ND	PD	ND
6.00	ND	ND	ND	ND	ND	ND
6.80	ND	ND	ND	ND	ND	ND
7.50	ND	ND	ND	ND	ND	ND

Legend: ( ) - Actual rain sample from Toyota plant.

D - Detectable damage to paint.

PD - Possible damage to paint (inspectors disagree).

ND - No detectable damage to paint.

Note: The wax coating thicknesses (from two tests for each paint color):

Dark Blue - 5.8 to 6.1 microns

White - 6.0 to 6.1 microns

Light Blue - 4.3 to 6.3 microns

TABLE 4.3 72-HOUR SOAKING TEST (110 °F)

pH	(WASHED)			(UNWASHED)		
	D BLUE	WHITE	L BLUE	D BLUE	WHITE	L BLUE
2.26	D	D	D	D	D	D
2.50	D	D	D	D	D	D
3.20	ND	PD	PD	ND	D	D
(3.58)	ND	ND	ND	ND	PD	ND
3.70	ND	ND	ND	ND	ND	ND
(3.71)	PD	ND	ND	ND	ND	ND
(4.40)	ND	ND	ND	ND	ND	PD
(4.60)	ND	ND	ND	ND	ND	ND
5.00	ND	ND	ND	ND	ND	ND
6.00	ND	ND	ND	ND	ND	ND
6.80	ND	ND	ND	ND	ND	ND
7.50	ND	ND	PD	ND	ND	ND

Legend: ( ) - Actual rain sample from Toyota plant.

D - Detectable damage to paint.

PD - Possible damage to paint (inspectors disagree).

ND - No detectable damage to paint.

Note: The wax coating thicknesses (from two tests for each paint color):

Dark Blue - 5.8 to 6.1 microns

White - 6.0 to 6.1 microns

Light Blue - 4.3 to 6.3 microns

TABLE 4.4 120-HOUR SOAKING TEST (110 °F)

pH	(WASHED)			(UNWASHED)		
	D BLUE	WHITE	L BLUE	D BLUE	WHITE	L BLUE
2.26	D	ND	D	D	D	D
2.50	D	ND	D	D	D	D
3.20	D	ND	D	ND	ND	ND
(3.58)	PD	ND	ND	ND	ND	ND
3.70	ND	ND	ND	ND	ND	PD
(3.71)	PD	ND	ND	ND	ND	PD
(4.40)	ND	ND	PD	ND	ND	PD
(4.60)	ND	ND	ND	ND	ND	PD
5.00	ND	ND	PD	ND	ND	PD
6.00	ND	ND	ND	ND	ND	PD
6.80	PD	ND	ND	ND	ND	PD
7.50	ND	ND	ND	ND	ND	ND

Legend: ( ) - Actual rain sample from Toyota plant.

D - Detectable damage to paint.

PD - Possible damage to paint (inspectors disagree).

ND - No detectable damage to paint.

Note: The wax coating thicknesses (from two tests for each paint color):

Dark Blue - 5.8 to 6.1 microns

White - 6.0 to 6.1 microns

Light Blue - 4.3 to 6.3 microns

TABLE 4.5 168-HOUR SOAKING TEST (110 °F)

pH	(WASHED)			(UNWASHED)		
	D BLUE	WHITE	L BLUE	D BLUE	WHITE	L BLUE
2.26	D	D	D	D	D	D
2.50	D	PD	D	D	D	D
3.20	PD	ND	ND	D	ND	ND
(3.58)	ND	ND	ND	ND	ND	ND
3.70	ND	ND	ND	ND	ND	ND
(3.71)	ND	ND	ND	ND	ND	ND
(4.40)	ND	ND	ND	ND	ND	ND
(4.60)	ND	ND	ND	ND	PD	ND
5.00	ND	ND	ND	ND	ND	ND
6.00	ND	ND	ND	ND	PD	ND
6.80	ND	ND	ND	ND	PD	ND
7.50	ND	ND	ND	ND	ND	ND

Legend: ( ) - Actual rain sample from Toyota plant.

D - Detectable damage to paint.

PD - Possible damage to paint (inspectors disagree).

ND - No detectable damage to paint.

Note: The wax coating thicknesses (from two tests for each paint color):

Dark Blue - 5.8 to 6.1 microns

White - 6.0 to 6.1 microns

Light Blue - 4.3 to 6.3 microns

TABLE 4.6 336-HOUR SOAKING TEST (110 °F)						
pH	(WASHED)			(UNWASHED)		
	D BLUE	WHITE	L BLUE	D BLUE	WHITE	L BLUE
2.26	D	D	D	D	D	D
2.50	D	D	D	D	D	D
3.20	ND	PD	ND	ND	D	D
(3.58)	ND	ND	ND	ND	ND	ND
3.70	ND	ND	ND	ND	ND	ND
(3.71)	ND	ND	ND	ND	ND	ND
(4.40)	ND	ND	PD	ND	ND	ND
(4.60)	ND	ND	PD	ND	ND	ND
5.00	ND	ND	ND	ND	ND	ND
6.00	ND	ND	PD	ND	ND	ND
6.80	ND	ND	ND	ND	ND	ND
7.50	ND	ND	PD	ND	ND	ND

Legend: ( ) - Actual rain sample from Toyota plant.

D - Detectable damage to paint.

PD - Possible damage to paint (inspectors disagree).

ND - No detectable damage to paint.

Note: The wax coating thicknesses (from two tests for each paint color):

Dark Blue - 5.8 to 6.1 microns

White - 6.0 to 6.1 microns

Light Blue - 4.3 to 6.3 microns

TABLE 4.7 CONTROL RESULTS, 150°F SOAK TESTS

pH	D BLUE	WHITE	L BLUE
2.26	D	D	D
2.50	D	D	D
3.20	ND	D	ND
(3.58)	ND	ND	ND
3.70	ND	ND	ND
(3.71)	ND	ND	ND
(4.40)	ND	ND	ND
(4.60)	ND	ND	ND
5.00	ND	ND	ND
6.00	ND	PD	ND
6.80	PD	ND	ND
7.50	ND	ND	ND

Legend: ( ) - Actual rain sample from Toyota plant.

D - Detectable damage to paint.

PD - Possible damage to paint (inspectors disagree).

ND - No detectable damage to paint.

Note: The wax coating thicknesses (from two tests for each paint color):

Dark Blue - 5.8 to 6.1 microns

White - 6.0 to 6.1 microns

Light Blue - 4.3 to 6.3 microns

TABLE 4.8 24-HOUR SOAKING TEST (150°F)						
pH	(PRE-WASHED)			(UNWASHED)		
	D BLUE	WHITE	L BLUE	D BLUE	WHITE	L BLUE
2.26	D	D	D	D	D	D
2.50	D	D	D	D	D	D
3.20	ND	ND	ND	PD	ND	D
(3.58)	ND	ND	ND	ND	ND	ND
3.70	ND	ND	ND	ND	ND	ND
(3.71)	ND	ND	ND	ND	ND	ND
(4.40)	ND	ND	ND	ND	ND	ND
(4.60)	ND	ND	ND	ND	ND	ND
5.00	ND	ND	ND	ND	ND	ND
6.00	ND	PD	ND	ND	ND	ND
6.80	ND	ND	ND	ND	ND	ND
7.50	ND	ND	ND	ND	ND	ND

Legend:	( ) - Actual rain sample from Toyota plant.
	D - Detectable damage to paint.
	PD - Possible damage to paint (inspectors disagree).
	ND - No detectable damage to paint.

Note: The wax coating thicknesses (from two tests for each paint color):

Dark Blue - 5.8 to 6.1 microns

White - 6.0 to 6.1 microns

Light Blue - 4.3 to 6.3 microns

TABLE 4.9 72-HOUR SOAKING TEST (150°F)

pH	(WASHED)			(UNWASHED)		
	D BLUE	WHITE	L BLUE	D BLUE	WHITE	L BLUE
2.26	D	D	D	D	D	D
2.50	D	D	D	D	D	D
3.20	ND	ND	D	D	ND	D
(3.58)	ND	ND	ND	D	PD	ND
3.70	ND	ND	ND	ND	ND	ND
(3.71)	ND	ND	PD	ND	ND	ND
(4.40)	ND	ND	ND	ND	ND	ND
(4.60)	ND	ND	ND	ND	ND	ND
5.00	ND	ND	ND	ND	ND	ND
6.00	ND	ND	ND	ND	ND	ND
6.80	ND	ND	ND	ND	ND	ND
7.50	ND	ND	ND	ND	ND	ND

Legend: ( ) - Actual rain sample from Toyota plant.

D - Detectable damage to paint.

PD - Possible damage to paint (inspectors disagree).

ND - No detectable damage to paint.

Note: The wax coating thicknesses (from two tests for each paint color):

Dark Blue - 5.8 to 6.1 microns

White - 6.0 to 6.1 microns

Light Blue - 4.3 to 6.3 microns

TABLE 4.10 120-HOUR SOAKING TEST (150 °F)

pH	(WASHED)			(UNWASHED)		
	D BLUE	WHITE	L BLUE	D BLUE	WHITE	L BLUE
2.26	D	D	D	D	D	D
2.50	D	D	D	D	D	D
3.20	D	D	ND	D	PD	ND
(3.58)	ND	ND	ND	PD	ND	ND
3.70	ND	ND	D	ND	ND	ND
(3.71)	ND	ND	ND	ND	ND	D
(4.40)	ND	ND	ND	ND	ND	ND
(4.60)	ND	ND	ND	ND	ND	ND
5.00	ND	ND	ND	ND	ND	D
6.00	ND	ND	ND	ND	ND	ND
6.80	ND	ND	ND	ND	ND	ND
7.50	PD	ND	ND	ND	ND	ND

Legend: ( ) - Actual rain sample from Toyota plant.

D - Detectable damage to paint.

PD - Possible damage to paint (inspectors disagree).

ND - No detectable damage to paint.

Note: The wax coating thicknesses (from two tests for each paint color):

Dark Blue - 5.8 to 6.1 microns

White - 6.0 to 6.1 microns

Light Blue - 4.3 to 6.3 microns

TABLE 4.11 168-HOUR SOAKING TEST (150 °F)						
pH	(WASHED)			(UNWASHED)		
	D BLUE	WHITE	L BLUE	D BLUE	WHITE	L BLUE
2.26	D	D	D	D	D	D
2.50	D	D	D	D	D	D
3.20	D	ND	D	D	D	D
(3.58)	D	ND	ND	ND	ND	PD
3.70	ND	ND	ND	ND	ND	ND
(3.71)	ND	ND	ND	ND	ND	ND
(4.40)	ND	D	ND	ND	ND	ND
(4.60)	ND	ND	ND	ND	ND	ND
5.00	ND	ND	ND	ND	ND	PD
6.00	ND	ND	ND	ND	PD	ND
6.80	ND	ND	ND	ND	ND	ND
7.50	ND	ND	ND	ND	ND	ND

Legend: ( ) - Actual rain sample from Toyota plant.

D - Detectable damage to paint.

PD - Possible damage to paint (inspectors disagree).

ND - No detectable damage to paint.

Note: The wax coating thicknesses (from two tests for each paint color):

Dark Blue - 5.8 to 6.1 microns

White - 6.0 to 6.1 microns

Light Blue - 4.3 to 6.3 microns

TABLE 4.12 336-HOUR SOAKING TEST (150 °F)						
pH	(WASHED)			(UNWASHED)		
	D BLUE	WHITE	L BLUE	D BLUE	WHITE	L BLUE
2.26	D	D	D	D	D	D
2.50	D	D	D	D	D	D
3.20	ND	ND	D	D	D	D
(3.58)	ND	ND	ND	ND	ND	ND
3.70	ND	ND	ND	ND	D	D
(3.71)	ND	ND	ND	ND	PD	D
(4.40)	ND	ND	ND	ND	ND	ND
(4.60)	ND	ND	ND	ND	ND	ND
5.00	ND	ND	ND	ND	D	ND
6.00	ND	PD	ND	ND	PD	ND
6.80	ND	ND	ND	ND	ND	ND
7.50	ND	ND	ND	ND	ND	ND

Legend: ( ) - Actual rain sample from Toyota plant.

D - Detectable damage to paint.

PD - Possible damage to paint (inspectors disagree).

ND - No detectable damage to paint.

Note: The wax coating thicknesses (from two tests for each paint color):

Dark Blue - 5.8 to 6.1 microns

White - 6.0 to 6.1 microns

Light Blue - 4.3 to 6.3 microns

TABLE 4.13 CONTROL RESULTS, 170°F SOAK TESTS			
pH	**D BLUE**	**WHITE**	**L BLUE**
2.26	D	D	D
2.50	D	D	D
3.20	D	D	D
(3.58)	ND	ND	ND
3.70	ND	ND	ND
(3.71)	ND	ND	ND
(4.40)	ND	ND	D
(4.60)	ND	ND	ND
5.00	ND	ND	ND
6.00	ND	ND	ND
6.80	ND	ND	ND
7.50	ND	ND	ND

Legend: ( ) - Actual rain sample from Toyota plant.

D - Detectable damage to paint.

PD - Possible damage to paint (inspectors disagree).

ND - No detectable damage to paint.

Note: The wax coating thicknesses (from two tests for each paint color):

Dark Blue - 5.8 to 6.1 microns

White - 6.0 to 6.1 microns

Light Blue - 4.3 to 6.3 microns

TABLE 4.14 24-HOUR SOAKING TEST (170 °F)						
pH	(WASHED)			(UNWASHED)		
	D BLUE	WHITE	L BLUE	D BLUE	WHITE	L BLUE
2.26	D	D	D	D	D	D
2.50	D	D	D	D	D	D
3.20	D	PD	D	D	ND	D
(3.58)	ND	ND	ND	D	ND	D
3.70	PD	ND	ND	ND	ND	ND
(3.71)	ND	ND	ND	ND	ND	ND
(4.40)	ND	D	ND	PD	ND	ND
(4.60)	PD	ND	ND	ND	PD	ND
5.00	ND	ND	ND	ND	ND	ND
6.00	ND	ND	ND	ND	ND	ND
6.80	ND	ND	ND	ND	ND	ND
7.50	ND	ND	ND	ND	ND	ND

Legend: ( ) - Actual rain sample from Toyota plant.

D - Detectable damage to paint.

PD - Possible damage to paint (inspectors disagree).

ND - No detectable damage to paint.

Note: The wax coating thicknesses (from two tests for each paint color):

Dark Blue - 5.8 to 6.1 microns

White - 6.0 to 6.1 microns

Light Blue - 4.3 to 6.3 microns

TABLE 4.15 72-HOUR SOAKING TEST (170 °F)

pH	(WASHED)			(UNWASHED)		
	D BLUE	WHITE	L BLUE	D BLUE	WHITE	L BLUE
2.26	D	D	D	D	D	D
2.50	D	D	D	D	D	D
3.20	D	PD	D	D	D	D
(3.58)	D	ND	D	D	PD	ND
3.70	ND	ND	ND	ND	PD	ND
(3.71)	ND	ND	ND	PD	ND	ND
(4.40)	ND	ND	ND	ND	ND	ND
(4.60)	ND	ND	ND	D	ND	ND
5.00	ND	ND	ND	D	ND	ND
6.00	ND	ND	ND	ND	ND	ND
6.80	ND	ND	ND	ND	ND	ND
7.50	ND	ND	ND	ND	ND	ND

Legend: ( ) - Actual rain sample from Toyota plant.

D - Detectable damage to paint.

PD - Possible damage to paint (inspectors disagree).

ND - No detectable damage to paint.

Note: The wax coating thicknesses (from two tests for each paint color):

Dark Blue - 5.8 to 6.1 microns

White - 6.0 to 6.1 microns

Light Blue - 4.3 to 6.3 microns

TABLE 4.16 120-HOUR SOAKING TEST (170 °F)						
pH	(WASHED)			(UNWASHED)		
	D BLUE	WHITE	L BLUE	D BLUE	WHITE	L BLUE
2.26	D	D	D	D	D	D
2.50	D	D	D	D	D	D
3.20	D	D	D	D	D	D
(3.58)	D	ND	PD	D	ND	D
3.70	ND	PD	PD	ND	ND	PD
(3.71)	ND	PD	D	ND	ND	PD
(4.40)	PD	ND	ND	ND	ND	ND
(4.60)	ND	ND	ND	ND	ND	PD
5.00	PD	PD	PD	D	ND	PD
6.00	ND	ND	PD	PD	ND	ND
6.80	ND	PD	PD	ND	ND	PD
7.50	ND	ND	PD	ND	ND	PD

Legend: ( ) - Actual rain sample from Toyota plant.

D - Detectable damage to paint.

PD - Possible damage to paint (inspectors disagree).

ND - No detectable damage to paint.

Note: The wax coating thicknesses (from two tests for each paint color):

Dark Blue - 5.8 to 6.1 microns

White - 6.0 to 6.1 microns

Light Blue - 4.3 to 6.3 microns

TABLE 4.17 168-HOUR SOAKING TEST (170 °F)

pH	(WASHED)			(UNWASHED)		
	D BLUE	WHITE	L BLUE	D BLUE	WHITE	L BLUE
2.26	D	D	D	D	D	D
2.50	D	D	D	D	D	D
3.20	D	D	D	D	D	D
(3.58)	PD	PD	D	PD	D	D
3.70	ND	ND	ND	PD	PD	ND
(3.71)	ND	ND	D	D	PD	D
(4.40)	ND	ND	ND	ND	ND	ND
(4.60)	ND	ND	ND	ND	ND	ND
5.00	ND	ND	ND	ND	ND	ND
6.00	ND	ND	ND	ND	ND	ND
6.80	ND	ND	ND	ND	ND	ND
7.50	ND	ND	ND	ND	ND	ND

Legend: ( ) - Actual rain sample from Toyota plant.

D - Detectable damage to paint.

PD - Possible damage to paint (inspectors disagree).

ND - No detectable damage to paint.

Note: The wax coating thicknesses (from two tests for each paint color):

Dark Blue - 5.8 to 6.1 microns

White - 6.0 to 6.1 microns

Light Blue - 4.3 to 6.3 microns

TABLE 4.18 336-HOUR SOAKING TEST (170 °F)						
pH	(WASHED)			(UNWASHED)		
	D BLUE	WHITE	L BLUE	D BLUE	WHITE	L BLUE
2.26	D	D	D	D	D	D
2.50	D	D	D	D	D	D
3.20	D	D	D	D	D	D
(3.58)	D	D	D	D	D	D
3.70	ND	ND	ND	PD	ND	ND
(3.71)	ND	ND	ND	PD	ND	ND
(4.40)	ND	PD	ND	PD	PD	ND
(4.60)	ND	PD	ND	ND	ND	ND
5.00	ND	ND	ND	ND	ND	PD
6.00	ND	ND	ND	ND	ND	ND
6.80	ND	ND	ND	PD	ND	ND
7.50	ND	ND	ND	PD	ND	ND

Legend: ( ) - Actual rain sample from Toyota plant.

D - Detectable damage to paint.

PD - Possible damage to paint (inspectors disagree).

ND - No detectable damage to paint.

Note: The wax coating thicknesses (from two tests for each paint color):

Dark Blue - 5.8 to 6.1 microns

White - 6.0 to 6.1 microns

Light Blue - 4.3 to 6.3 microns

5. HUMIDITY LABORATORY TESTING

5.1 Test Objectives and Synopsis

5.1.1 Test Objectives

5.1.1.1 The humidity laboratory tests were performed to determine the effect of humidity on the acid rain damage. High humidity was expected to prevent evaporation and maintain long-term contact between the acid rain solution and the paint/wax. Elevated test temperatures were employed to simulate anticipated service temperatures.

5.1.1.2 To separate the effect of humidity from temperature, a series of tests was planned which would be conducted at high temperatures and humidities. A test design was planned whereby the specimens would be exposed to the acid rain solutions in sealed petri dishes. The bottom of the petri dishes would be filled with distilled water to maintain high humidities and the specimens would rest on shims to prevent their immersion and the dilution of the acid rain solutions. The tests would be conducted for periods in excess of the total exposure time of specimens to acid rain solutions during the cyclic evaporation tests (typically 15 minutes times 12 exposures or a total wetted time period of about 3 hours). The concentrations of acid acting on the wax (and paint) would be more dilute over the course of the test. Those tests would replicate field conditions involving rain or dew deposited on vehicle finishes, but not evaporating quickly due to high relative humidity. Waxed and unwaxed specimens were tested.

5.1.2 Test Synopsis

5.1.2.1 The humidity laboratory tests were performed by exposing a small drop of acid rain on the surface of a small paint/wax-coated specimen representing a vehicle exterior finish. The acid rain wetted specimens were placed in enclosed petri dishes that contained extra moisture. The petri dishes were placed in an oven and held at elevated temperatures for 4 hours. The excess moisture in the petri dishes prevented the acid rain solutions from evaporating. After the test, the specimens were removed from the oven, rinsed, and the wax was stripped from the test surface. The specimens were visually inspected for acid rain damage and the results were recorded.

5.2 Test Procedure

5.2.1 Preparation

1. Shear painted/waxed sheet metal furnished by Toyota Motor Manufacturing to form 1-inch square specimens. Protect the sheet metal from surface distress during shearing by covering with paper.

2. Employ a constant-temperature regulated oven. The oven is equipped with an ultraviolet light in a fixture approximately 5 inches from the test surface of the

specimens. Set the oven to the predetermined test temperature prior to starting a test.

3. Select waxed and unwaxed specimens for this test. Inspect the test surface to insure the paint/wax is in good condition. Mark the back face of the specimen for identification.

4. Divide the test surface into four sections with an oil-based marker.

5. Rinse the test surface of each specimen with distilled water.

5.2.2 Testing

1. Pour sufficient distilled water into a small petri dish to cover the bottom of the dish. Place the specimen in the dish. The specimen is placed in the petri dish on a plastic shim to prevent water from contacting the specimen test surface. Sufficient petri dishes are prepared to perform all necessary tests at a specific test temperature.

2. Coat the petri dish cap with petrolatum to provide a moisture sealant on its inner face and sealing flange. That will prevent water from falling on top of the specimen during the test and will retain the moisture inside the petri dish.

3. Deposit four drops of different pH values of acid rain solution on the test surface of each specimen. Each drop has a volume of 0.02 cc. It is measured and deposited from an 1-cc syringe. The drops are centered on the four sections of each 1 inch-square specimen.

4. Place a beaker of water in the oven.

5. The specimens are placed in the preheated oven. They are kept in the oven for 4 hours. Then, the specimens are removed and steps 1-5 are repeated using different specimens for the other 2 test temperatures.

5.2.3 Cleaning and Wax Removal

1. Wax is stripped using Yuma Industries **Yumage ST-210** wax remover. The specimen is immersed in a petri dish filled with the cleaner for 2 minutes. Then the specimen is removed and rinsed with distilled water.

2. The specimens are placed in petri dishes filled with distilled water and are ultrasonically cleaned for 5 minutes. Subsequently, they are rinsed with distilled water and air dried.

5.2.4 Inspection

1. All specimens tested at a specific temperature are mounted on a display board. The board is marked to identify the specimens by acid rain pH values, waxed or unwaxed, and temperature.

2. The specimens are visually inspected independently by two researchers. The specimens are inspected indoors under ultraviolet light. The researchers record whether or not they detect visible damage to the surface of the specimens on test sheets.

3. The two researchers compare their test sheets and re-inspect the specimens. If the researchers agree on the condition of the specimens, the final records will indicate ND (not damaged) or D (damaged). If the inspectors do not agree, the condition for a particular specimen will be recorded as PD (possible damage).

5.3 Test Parameters and Conditions

5.3.1.1 The test matrix for the series of tests covered humid conditions (100 percent relative humidity), three oven temperatures (110, 150, and 170 °F), three colors (white, light blue, and dark blue) which were waxed and unwaxed, and 12 acid rain or pH values. Eight of the pH solutions were made in a laboratory according to EPA guidelines (pH values of 2.25, 2.50, 3.20, 3.70, 5.00, 6.00, 6.80, and 7.50). The other four solutions (pH values of 3.58, 3.71, 4.40, and 4.60) were collected at the Toyota plant. During the soak tests, 216 specimens were tested. All specimen types (in terms of color and wax condition) and test conditions (in terms of temperature and pH solutions) were employed during this series of tests.

5.4 Profilometry

5.4.1 The wax coatings on the specimens were measured using the profilometry technique employed in 3.4.1.2. The wax coating thickness varied from 5.8 to 6.1 microns for light blue specimens, 6.0 to 6.1 microns for white specimens, and 4.3 to 6.3 microns for dark blue specimens.

5.5 Test Results

5.5.1 Visual Inspections

5.5.1.1 On removal of the specimens from the petri dishes, it was observed that none of the acid rain drops had evaporated. On cleaning, it was observed that the wax had been disturbed where the drops were located forming circular marks. In most cases, the underlying paint was observed to be undisturbed. Most of the unwaxed specimens did not reveal any deposits or damage.

5.5.2 Wax Coating/Paint Performance

5.5.2.1 The humidity test results are presented in Tables 5.1 to 5.3. Only four of the test specimens were determined to be damaged. Each of the damage specimens were unwaxed. Of those, two were damaged at 110 °F and one each were damaged at 150 and 170 °F.

5.5.2.2 Paint Damage Factors (described in Appendix 2) were assigned to the results of the humidity tests. The average values of the Paint Damage Factors were slightly higher for tests conducted at 110 and 170 °F than the average value of the 150 °F tests. The average value of the Paint Damage Factors for all the unwaxed tests was slightly higher than the average value for the waxed tests.

TABLE 5.1 4-HR HUMIDITY TESTS (110 °F)

pH	WAXED			UNWAXED		
	D BLUE	WHITE	L BLUE	D BLUE	WHITE	L BLUE
2.26	PD	ND	ND	ND	ND	ND
2.50	ND	PD	ND	ND	D	ND
3.20	ND	PD	ND	ND	ND	ND
(3.58)	ND	ND	ND	D	ND	PD
3.70	ND	PD	ND	ND	ND	ND
(3.71)	ND	PD	ND	ND	ND	ND
(4.40)	ND	ND	ND	ND	ND	PD
(4.60)	ND	ND	ND	ND	ND	PD
5.00	PD	ND	ND	ND	ND	ND
6.00	ND	ND	PD	PD	ND	PD
6.80	ND	ND	ND	ND	ND	ND
7.50	ND	ND	ND	ND	ND	ND

Legend:	( ) - Actual rain sample from Toyota plant.
	D - Detectable damage to paint.
	PD - Possible damage to paint (inspectors disagree).
	ND - No detectable damage to paint.

Note: The wax coating thicknesses (from two tests for each paint color):

Dark Blue - 5.8 to 6.1 microns

White - 6.0 to 6.1 microns

Light Blue - 4.3 to 6.3 microns

TABLE 5.2 4-HR HUMIDITY TESTS (150^{o}F)						
pH	WAXED			UNWAXED		
	D BLUE	WHITE	L BLUE	D BLUE	WHITE	L BLUE
2.26	ND	ND	ND	ND	ND	ND
2.50	ND	ND	ND	ND	D	ND
3.20	ND	ND	ND	ND	ND	ND
(3.58)	ND	ND	ND	PD	ND	ND
3.70	ND	ND	ND	ND	ND	ND
(3.71)	PD	ND	ND	ND	ND	ND
(4.40)	ND	ND	ND	ND	ND	ND
(4.60)	ND	ND	ND	ND	ND	ND
5.00	ND	ND	ND	ND	ND	ND
6.00	ND	ND	ND	ND	ND	ND
6.80	ND	ND	ND	ND	ND	ND
7.50	ND	ND	ND	ND	ND	ND

Legend: ( ) - Actual rain sample from Toyota plant.

D - Detectable damage to paint.

PD - Possible damage to paint (inspectors disagree).

ND - No detectable damage to paint.

Note: The wax coating thicknesses (from two tests for each paint color):

Dark Blue - 5.8 to 6.1 microns

White - 6.0 to 6.1 microns

Light Blue - 4.3 to 6.3 microns

TABLE 5.3 4-HR HUMIDITY TESTS (170°F)						
pH	WAXED			UNWAXED		
	D BLUE	WHITE	L BLUE	D BLUE	WHITE	L BLUE
2.26	ND	ND	ND	PD	ND	ND
2.50	ND	PD	PD	PD	ND	PD
3.20	ND	ND	PD	PD	ND	PD
(3.58)	ND	ND	PD	PD	ND	ND
3.70	PD	ND	ND	ND	ND	ND
(3.71)	ND	ND	ND	ND	PD	PD
(4.40)	PD	ND	ND	PD	PD	ND
(4.60)	ND	ND	ND	ND	ND	PD
5.00	ND	ND	ND	D	PD	PD
6.00	ND	ND	PD	ND	PD	PD
6.80	ND	ND	ND	PD	ND	ND
7.50	ND	ND	ND	ND	ND	ND

Legend: ( ) - Actual rain sample from Toyota plant.

D - Detectable damage to paint.

PD - Possible damage to paint (inspectors disagree).

ND - No detectable damage to paint.

Note: The wax coating thicknesses (from two tests for each paint color):

Dark Blue - 5.8 to 6.1 microns

White - 6.0 to 6.1 microns

Light Blue - 4.3 to 6.3 microns

6. FIELD EXPOSURE TESTING

6.1 Test Objectives and Synopsis

6.1.1 Test Objectives

6.1.1.1 The purpose of the field tests was to determine the effect of long-term field exposure at the Toyota marshalling yard on the performance of waxed specimens exposed to acid rain deposition and evaporation. The tests were restricted to light-blue specimens. If these tests had been performed during warmer periods of the year, the acid rain damage would probably be more severe. Field exposure tests were initiated on September 29, 1990 and terminated on November 29, 1990. Temperatures were moderate at that time. The duration of the tests was set at 10 weeks which UK researchers believed represented extended vehicle storage at the marshalling yard. To determine the effect of the duration of field exposure, sets of equivalent specimens were exposed to similar acid rain solutions. Those specimens were exposed at the same time. The sets were removed for cleaning and inspection at fixed intervals.

6.1.2 Test Synopsis

6.1.2.1 Prior to the field exposure tests, small drops of acid rain were placed on the surface of small paint/wax-coated specimens and evaporated at 150 °F in the laboratory. The specimens were placed in the field at the Toyota marshalling yard, on the roof of the VPI building. Sets of equivalent specimens were removed at 1-week intervals. The specimen sets were subsequently cleaned and inspected for acid rain damage.

6.2 Test Procedure

6.2.1 Preparation

1. Shear painted/waxed sheet metal furnished by Toyota Motor Manufacturing to form 1-inch square specimens. Protect the sheet metal from surface distress during shearing by covering with paper.

2. Employ constant-temperature regulated oven. The oven is equipped with an ultraviolet light in a fixture approximately 5 inches from the test surface of the specimens. Set the oven to the test temperature 15 minutes prior starting a test.

3. Use ambient humidity in test facility during test.

4. Select light blue waxed specimens to be used for this test. Inspect the test surface to insure the paint/wax is in good condition. Mark the back face of the specimens for identification.

5. Divide the test surface into four sections with an oil-based marker.

6. Rinse the test surface of each specimen with distilled water.

6.2.2 Testing

1. Deposit four drops of different pH values of acid rain solution on the test surface of each specimen. Each drop has a volume of 0.02 cc. It is measured and deposited from an 1-cc syringe. The drops are centered on the four sections of each 1-inch square specimen.

2. Thirty light blue waxed test specimens are placed on a tray to be tested at 150 °F. Each marked specimen is wetted with drops of the designated acid rain solutions. The time between initial wetting and evaporation of the drops in the oven is limited to the time required to place drops on all the specimens to be tested.

3. The specimens are placed in the warmed oven. They are kept in the oven until the drops evaporate. During this phase of the test, the specimens are inspected at 5-minute intervals to determine when the drops have evaporated. Once the drops have evaporated on all the specimens (about 15 minutes), the tray is removed from the oven.

4. The specimens are removed from the tray, rinsed with tap water, and allowed to air dry.

5. The specimens are mounted on small rectangular plexiglass plates. Each plate contains three specimens and represents one-week exposure time. The board is placed on a rooftop at the Toyota plant. One plate is removed on a weekly basis for 10 weeks.

6.2.3 Cleaning and Wax Removal

1. The wax coating is stripped with Yuma **Yumage ST-210** wax remover. The specimens are immersed in a petri dish filled with the cleaner for 2 minutes. Then, they are rinsed with distilled water.

2. The specimens are placed singly in petri dishes filled with distilled water. They are ultrasonically cleaned for 5 minutes and subsequently rinsed with distilled water and air dried.

6.2.4 Inspection

1. All specimens are mounted on a display board. Specimen locations are determined by pH value and exposure duration.

2. The specimens are visually inspected independently by two researchers. The specimens are inspected indoors under ultraviolet light. The researchers record whether they detect damage to the specimens.

3. The two researchers compare their test sheets and re-inspect the specimens. If the researchers agree on the condition of the specimens, the final records will indicate ND (not damaged) or D (damaged). If the inspectors do not agree, the condition for a particular specimen will be recorded as PD (possible damage).

6.3 Test Parameters and conditions

6.3.1 The test matrix for the series of tests covered 10 sets of specimens with field exposures ranging from 1 to 10 weeks, one paint color (light blue), waxed specimens, and 12 acid rain pH values. Eight of the pH solutions were made in a laboratory according to EPA guidelines (pH values of 2.25, 2.50, 3.20, 3.70, 5.00, 6.00, 6.80, and 7.50). The other four solutions (pH values of 3.58, 3.71, 4.40, and 4.60) were collected at the Toyota plant. These values are listed on the test data sheets in this report. During the field exposure tests, 120 individual tests were performed.

6.4 Profilometrey

6.4.1 The wax coatings on the specimens were measured using the profilometry technique employed in 3.4.1.2. The wax coating thickness for the light blue specimens varied from 4.3 to 6.3 microns.

6.5 Test Results

6.5.1 Visual Inspections

6.5.1.1 On removal of the specimens from the field site, typical circular crustaceous deposits were observed where low pH acid rain solutions had been placed. Additionally, small spots were observed on other specimens where no acid rain spots were anticipated.

6.5.2 Wax Coating/Paint Performance

6.5.2.1 The test results are provided in Table 6.1. Damage was detected for specimens in each week of exposure. Damage to the specimens increased noticeably after the seventh week. The most damaged specimens were detected in the final week when 10 of the 12 pH test samples exhibited damage. The test samples at pH values 3.20 and less had higher incidence of damage (87 percent) than tests at higher pH values (20 percent).

6.5.2.2 Trends for field exposure test data were discerned by quantitative analyses presented in Appendix 2, Figure 26. There was a trend toward increased damage to specimens with increased field exposure.

TABLE 6.1 FIELD EXPOSURE TESTS AT TOYOTA GEORGETOWN PLANT

pH	EXPOSURE TIME (WEEKS)									
	1	2	3	4	5	6	7	8	9	10
2.26	D	D	D	D	D	D	D	D	D	D
2.50	D	D	PD	D	D	D	D	D	D	D
3.20	D	PD	PD	D	D	PD	D	D	D	D
(3.58)	D	ND	PD	D	PD	ND	ND	D	ND	D
3.70	ND	ND	D	ND	ND	ND	ND	D	ND	D
(3.71)	ND	ND	PD	ND	PD	PD	ND	D	D	D
(4.40)	ND	ND	ND	ND	D	ND	ND	PD	ND	D
(4.60)	ND	ND	ND	ND	ND	PD	PD	ND	ND	D
5.00	ND	ND	ND	ND	D	PD	ND	D	ND	ND
6.00	ND	ND	ND	ND	PD	D	ND	ND	ND	D
6.80	ND	ND	ND	ND	PD	PD	ND	ND	PD	PD
7.50	ND	ND	ND	ND	ND	ND	PD	ND	PD	D

Legend: ( ) - Actual rain sample from Toyota plant.

D - Detectable damage to paint.

PD - Possible damage to paint (inspectors disagree).

ND - No detectable damage to paint.

Note: The wax coating thickness for the light blue paint used for the field exposure tests ranges from 4.3 to 6.3 microns based on tests of two specimens.

7. pH MICROPROBE

7.1 Description and Operation

7.1.1 Description

7.1.1.1 UK researchers desired to test the pH of rain drops on vehicle surfaces during evaporation. That required a reference electrode capable of providing accurate readings of very small liquid volumes. A suitable electrode, the **M-410 Micro-Combination pH Electrode**, manufactured by Microelectrodes Inc. of Londonderry, New Hampshire provided the capability of accurately measuring pH values in volumes down to 0.005 cc. The electrode consisted of a half cell of silver wire in a potassium chloride solution. It had two wire leads and a tubular glass body approximately 6 inches long and 0.25 inches in diameter. The glass was drawn to a fine tip at the electrode end and the silver wire was barely exposed at its tip. The electrode was compatible with common BNC connected pH meters, but required a separate probe for temperature compensation of pH values. A Beckman **Φ 10 pH Meter**, portable battery-powered unit was purchased along with a Beckman **598115 Automatic Temperature Compensator Probe**. That unit was intended to be used for field tests. Specifications for the microprobe are provided in Appendix 5.

7.1.2 Operation

7.1.2.1 Calibration (Two-standard method)

1. Clean two small beakers with distilled water and dry thoroughly. Pour a small amount of pH 4.00 buffer solution into one cleaned beaker and a small amount of pH 7.00 buffer solution into the other one.

2. Use tap water for electrode rinse.

3. Standardize the pH meter provided with the two buffer solutions previously mentioned.

4. Prepare the sample to be tested. If conducting laboratory test, put a drop of the sample on a cleaned hard surface such as a sheet of glass. Field test require no sample or surface preparation when using the pH microprobe.

5. Remove the tape that secures the pH microprobe in its glass tube. Save the tape for reuse. Remove the microprobe from the tube. The white sleeve which covers the fill hole is moved down the glass tube to ventilate the reference chamber before testing.

7.1.2.2 Testing

1. Put a droplet of the unknown pH solution on the test surface.

2. Hold the microprobe in an upright position and touch the surface of the test droplet. Record the pH value indicated on the pH meter.

8. FUTURE WORK

8.1 Laboratory Testing

8.1.1 Additional laboratory tests will better characterize coating performance. UK researchers have acquired a rudimentary understanding of the acid rain susceptibility of both transient coatings and paints. That basic understanding should be expanded and further progress should be made in studying in acid rain behavior.

8.1.2 The following topics warrant further research:

1. Effect of (same pH) sulfate to nitrate ratio on damage -
Toyota personnel presently use pH values as the sole indicator of acid rain damage potential. Evidence exists that indicates that the sulfate to nitrate ratio is also important and this should be evaluated.

2. Specific damage mechanisms -- etching vs smudging vs leaching, etc -
Further investigations of specific damage mechanisms may provide insight into developing better paints, transient coatings, and protection procedures.

3. Controlled wax thickness -
The present research did not directly address the quantitative effect of wax thickness. The wax coating presently employed by Toyota is at least partially effective in mitigating the damaging effect of acid rain, but the thickness varies. Would increased coating thickness or more consistent coating thickness provide better protection?

4. Formalized test procedures and parameters for future performance testing -
The tests and procedures developed under this program provide the basis for accelerated performance of new paints and protective coatings. Those tests will adequately characterize the field performance of new paints and coatings.

5. Statistically valid damage tests to set firm base lines for paint and wax coating acid rain resistance -
This is an adjunct to item 4. above. A start has been made toward achieving this goal by the development of a quantitative analysis procedure to rate coating performance.

8.2 Field Testing

8.2.1 The greatest shortfall in progress desired by UK researchers was in performing field monitoring tests. It should be noted that the weather in the Central Kentucky area was moderate during the course of the program and was not conducive to acid rain damage.

8.2.2 The following topics warrant further research:

1. Effect of aging under site conditions on efficacy of transient coatings - It is to be expected that the protective properties of the transient coating will change with time. Temperature is expected to have strong influence on that change. Stripping of transient coatings at the destinations may also be affected. This issue should be addressed in a coherent manner.

2. pH during evaporation of rain drop on surface - The pH microprobe purchased during this program was not used at the Toyota marshalling yard. It has been used successfully in the laboratory. The microprobe should be used in the forthcoming summer months at the Toyota marshalling yard to evaluate how the pH of rain drops vary during evaporation.

3. Extended field exposure tests and monitoring - Further field exposure tests should be conducted over the next 3 years in anticipation of severe weather patterns (in the acid rain damage sense) at the Toyota marshalling yard. More severe weather has occurred in the last 5 years and may well re-occur in the next 3 years. Work would be performed to correlate laboratory and field tests.

8.3 Early Warning Capability

8.3.1 Develop an early warning capability for the occurrence of severe air pollution episodes. Due to the recent development of real-time, regional-scale meteorological prediction models, it is now feasible to construct a regional-scale air pollution numerical model that would be able to provide an early warning of the possible occurrence of severe air pollution episodes. The ultimate goal of the project would be to develop a numerical modeling system that would provide a daily "prediction" of local air quality for the succeeding 24-36 hrs. The so-called "prediction" obtained from the modeling system would be similar in nature to a typical weather forecast; e.g., 50% chance of showers with a 25% chance of rainfall pH<4.0. Although the development of such an air quality modeling system is now feasible, considerable effort will have to be expended before a reliable predictive capability is achieved. It is expected that a working preliminary modeling system could be in place after 1 year, while "tuning" of the models to provide reliable predictions could take 1 to 2 additional seasonal cycles, thus requiring a total project period of 2 to 3 years. That system would allow proactive planning and preparation to minimize the damaging effects of low-pH acid rain events.

8.4 Further UK Participation in the Protective Coating Program

8.4.1 UK researchers have been informed that the Kentucky Transportation Cabinet will sponsor research related to performance and evaluation of EPA-compliant paints at the Kentucky Transportation Center over the next 3 to 5 years. That work may prove complimentary to Toyota transient coating and paint requirements. Additionally, UK researchers have extensive facilities at CAER and on the main campus to further explore transient coating and paint performance and mechanistic properties of acid rain attack. Those resources can be applied to further research in this or related fields. UK researchers also have an interest in being members in any larger acid rain program Toyota Motor Manufacturing may establish.

9. DISCUSSIONS AND CONCLUSIONS

9.1 Discussion

9.1.1 Laboratory Observations

1. The most typical acid rain damage is etching caused by corrosive attack to the paint by acids in the test solutions. That damage is revealed either as concentric rings or as random pits in the surface of the paint.

2. In some cases, acid rain damage is revealed as surface deposits. That can be due to crazing of the paint surface, leaching of certain paint compounds, or deposition of solids from the acid rain solutions/particulate interactions. That damage can occur concurrently with etching.

3. In other instances, acid rain damage causes fine damage (disturbance) to the paint surface that is only detectable under a microscope. The fine damage appears to be affected by the application of the paint remover. That damage has sometimes been confused with normal imperfections in the paint. However, it detracts from the quality of paint appearance, though not as readily as etching or surface deposits. It is normally detected as dark smudging, non-uniform surface sheen, or spotting in metal-flake paints.

4. The first inspections of a hood from the initial batch of Camrys indicated to UK researchers that if acid rain deposits are not eliminated, they will continue to damage the paint finish. Continued exposure to that damage will result in rusting.

9.1.2 Field Observations

9.1.2.1 Some field exposure specimens showed evidence of slight pitting. That damage was evident on specimens exposed for extended time periods. Initially, UK researchers believed that the pits were paint flaws. Microscopic inspection revealed that the pits had similar details to etching damage caused by acid rain exposure. That lead UK researchers to conclude the damage was exposure related.

9.1.2.2 At the invitation of Toyota personnel, UK researchers inspected unpainted hoods damaged in tests at the Toyota site. Visual inspection of naturally occurring damage indicated it was etching similar to that obtained in laboratory tests with one exception: the field damage (etching) was not in circular shapes normally generated when depositing drops of acid rain on the test surface. Those shapes were more irregular and were similar to those on the early damaged Camry hood that Toyota furnished to UK researchers. During the same visit, UK researchers observed copious amounts of dew on flat surfaces of the stored vehicles. The temperature was cold that day and the dew was observed and collected at about 10:30 A.M. The pH of the dew was 5.5. The role of acid dew in degradation of the transient coating and damage to the paint needs to be considered further. This can be done during the field evaluation testing phase of the proposed new work.

9.1.3 Attendant Work by Others

9.1.3.1 UK researchers have reviewed several cognizant articles and reports by others (Appendix 1, Reference 1-3). The literature on acid rain damage to vehicle finishes is sparse and much related research may be proprietary. A literature search conducted for this program is contained in Appendix 1. In reviewing the literature, it is evident that crustaceous deposits may form during acid rain/paint or transient coating interactions. Those deposits may make the interaction more visible to the untrained eye. Such deposits may be superficial, but research indicates that such deposits accompany underlying etching-type damage. During laboratory tests, the cleaning process employed removed much of the crustaceous deposits and in inspecting for damage, UK researchers wound up only inspecting for signs of etching. A comparison of knowledge gained in this program compared to relying solely on field tests (as done by other researchers) indicates that without controlled laboratory experiments, one can only guess at causal relationships in evaluating field test data. There are simply too many variables to derive basic relationships by conducting field tests. Proper evaluations of data from careful laboratory tests will promote better understanding of fundamental relationships and allow the preparation and conduct of meaningful field experiments.

9.2 Conclusions

9.2.1 Transient Wax Evaluation

9.2.1.1 Results for all laboratory tests, waxed and unwaxed indicate that acid rain damage is primarily a function of the pH of the acid rain solution (Appendix 2, Figure 27). The experiments conducted during this program reveal that the Yuma Industries **YUMAX SR-10** water based acrylic resin coating provides a measure of protection to the current paints used by Toyota Motor Manufacturing throughout the range of acid rain solutions tested (Appendix 2, Figure 28). The amount of protection decreases as the pH decreases. The coating appears to be satisfactory to prevent damage from moderately acidic rains and dews. However, the amount of acid-rain protection does not appear to be significant when the pH is lower than 4.0.

9.2.2 Washing Stored Vehicles after Acid Rains

9.2.2.1 The current practice of washing vehicles after acid rains having pH values less than 4.0 appears to have a slight benefit. Laboratory testing shows that benefit could be increased greatly by washing before the acid rain evaporates. If that is not practical, consideration might be given to adding a mild buffer, such as sodium bicarbonate, to the wash solution.

9.2.3 Temperature, Color, and Test Type

9.2.3.1 Test temperature, paint color, and test type all appear to effect the susceptibility of the paint to damage (Appendix 2, Figures 29-31). The laboratory tests appear to be more severe than the field exposure tests. That may or may not be beneficial in employing those laboratory tests to determine paint or transient coating suitability.

9.2.4 Evaporation and Damage

9.2.4 In most tests, paint damage occurred due to the evaporation-to-dryness of the acid rain solutions. Evaporation appears to play an important role in the damage process.

APPENDIX 1

(Literature Search)

Bibliography

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6. Tudor, W. F., "Automotive Challenges to the Finishing Industry," Society of Automotive Engineers, 1980.

Dialog Literature Search
Conducted by Laura Whayne, Librarian
Kentucky Transportation Center
February 1, 1990

Dialog Databases Searched

TRIS (file 63) Transportation Research Information Services. U.S. Department of Transportation and the Transportation Research Board.

NTIS (file 6) National Technical Information Service.
U.S. Department of Commerce.

POLLUTION ABSTRACTS (file 41) Cambridge Scientific Abstracts.

ENVIROLINE (file 40) R. R. Bowker.

COMPENDEX PLUS (file 8) Engineering Information, Inc. (file 8) Engineering Information, Inc.

Titles and Descriptors

Note: Bold-faced titles appear in the bibliography

The 'Title' and 'Descriptor' fields of the TRIS database were searched using the following terms:

ACID RAIN OR ACID PRECIPITATION OR ACID DEPOSITION OR SULFATE(S)
Results: 547 Records found, Records 1-10 listed below:

Gasoline Sulfur Control May be Required...or Sulfate Emissions Problems May Arise with Three-Way Catalyst Systems (525933) file 63. TRIS

The Role of Rhodium in RH/PT Rhodium/Platinum Catalysts for CO/HC/NOX and SO4 Carbon Monoxide/Hydrocarbon/Nitrogen Oxides, and Sulfate Emission Control: The Influence of Oxygen on Catalyst Performance (524458) file 63. TRIS

Dynamics of Automotive Sulfate Emissions: Interim Report (524306) file 63. TRIS

Sulfate Emissions from Vehicles on the Road (523851) file 63. TRIS

Managed Secondary Air: A Means of Achieving Sulfate Emission Control with Catalyst Equipped Vehicles (523293) file 63. TRIS

Evaluation of Sulfate Trapping Candidates: Results from Dynamometer and Vehicle Screening Tests (522669) file 63. TRIS

Automotive Sulfate Emissions: A Baseline Study (522017) file 63. TRIS

Effects of Engine Parameters and Catalyst Composition on Vehicle Sulfate Emissions (522016) file 63. TRIS

Effect of Catalyst Operating History on Sulfate Emissions (519262) file 63. TRIS

The GM Sulfate Dispersion Experiment: Reducing Uncertainties About the Catalytic Converter (519063) file 63. TRIS

PAINT(S) OR FINISH(ES) OR PROTECTIVE COATING(S)

Results: 3242 Records found, Records 1-10 listed below:

Evaluation of Protective Coatings to Reduce Chloride Penetration of Bridge Surfaces (553744) file 63. TRIS

Korea Chemical and Kochiam Add the Finishing Touch (552825) file 63. TRIS

Equipment Leasing (552171) file 63. TRIS

Paints and Coatings (552131) file 63. TRIS

Harnessing the Power (551640) file 63. TRIS

NTTC Chairman Robert Shertz Paints Harsh Tank Carrier Economic Picture (551558) file 63. TRIS

Engines, Paints: Owners Still Emphasizing Low Cost Efficiency (550934) file 63. TRIS

Benjamin Moore and Company's Private Fleet: Using Service to Paint a Bright Future (550731) file 63. TRIS

Analysis of Selected Automotive Parts and Assemblies for Cost and Material Impacts (531128) file 63. TRIS

Advanced Headlighting Systems (530788) file 63. TRIS

[ACID RAIN OR ACID PRECIPITATION OR ACID DEPOSITION OR SULFATE(S)] AND [PAINT(S) OR FINISH(ES) OR PROTECTIVE COATING(S)] AND [AUTOMOBILE(S) OR VEHICLE(S) OR MOTOR VEHICLE(S)]

Results: 2 Records found and listed below:

Road Tests of Traffic Paints (21668) file 63. TRIS

Overview and Review of Motor Gasoline Desulfurization. Volume 1 (168598) file 63. TRIS

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The 'Title', 'Descriptor', and 'Abstract' fields of the TRIS
database were searched using the following terms:

[ACID RAIN OR ACID PRECIPITATION OR ACID DEPOSITION OR SULFATE(S) OR AIR POLLUTION] AND [PAINT(S) OR FINISH(ES) OR PROTECTIVE COATING(S)] AND [AUTOMOBILE(S) OR VEHICLE(S) OR MOTOR VEHICLE(S)]
Results: 20 Records found and listed below:

Cars Go Rusty: An Analysis of Certain Types of Corrosion in Passenger Cars (513457) file 63. TRIS

Reactions Between Vehicle Emissions and Building Materials (377998) file 63. TRIS

Automotive Paint System Hydrocarbon Control at a Practical Cost (345197) file 63. TRIS

Automotive Manufacturing Processes: Volume I - Overview (337161) file 63. TRIS

Automotive Challenges to the Finishing Industry (513457) file 63. TRIS

Shopping for New Coats (325016) file 63. TRIS

An Economic and Technical Appraisal of Air Pollution in the United Kingdom (240387) file 63. TRIS

Lead in the Rural Environment and Lead in the Urban Environment (224507) file 63. TRIS

Maybe It's Not Goodbye Paint, But It's Certainly Hello Powder Coating (217215) file 63. TRIS

Protective Coatings for Highway Structural Steel (216923) file 63. TRIS

Road Tests of Traffic Paint (216668) file 63. TRIS

Environmental Contamination by Lead and Other Heavy Metals (186782) file 63. TRIS

Epidemiologic Study of the Effects of Automobile Traffic on Blood Lead Levels (186679) file 63. TRIS

Environmental Determinants of Lead Burdens in Children (185878) file 63. TRIS

Gasohol if Tested (178872) file 63. TRIS

A Study of Methods for Reducing Evaporative Background Hydrocarbon Emissions (168704) file 63. TRIS

Overview and Review of Motor Gasoline Desulfurization: Volume I (168598) file 63. TRIS

Accelerated Decay of Non-Fuel Evaporative Emissions (150967) file 63. TRIS

A Program for Safe Cyclomuting (128565) file 63. TRIS

Final Report for State Wide Emissions Inventory for the State of Louisiana (041791) file 63. TRIS

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The 'Title', 'Descriptor', and 'Abstract' fields of the NTIS, Pollution Abstracts, Enviroline, and Compendex Plus databases were searched using the following terms:

[ACID RAIN OR ACID PRECIPITATION OR ACID DEPOSITION OR SULFATE(S) OR AIR POLLUTION] AND [PAINT(S) OR FINISH(ES) OR PROTECTIVE COATING(S)] AND [AUTOMOBILE(S) OR VEHICLE(S) OR MOTOR VEHICLE(S)]

Results: 93 Records found. Listed below are records 1-10, 35-39, 87-93, 40-49 (First 10 records from each file); and records 50-86 (Records 11-47 from file 8 Compendex Plus):

Supplementary Measures to Reduce Emissions on a Medium-Sized Passenger Vehicle (1423661) file 6. NTIS

Praxiserprobung eines schadstoffarmen Fahrzeugs durch Anwendung konventioneller technischer Massnahmen (1415196) file 6. NTIS *German*

Protocol for Determining the Daily Volatile Organic Compound Emission Rate of Automobile and Light-Duty Truck Topcoat Operations (1380315) file 6. NTIS

Reduction of Volatile Organic Compound Emissions From Automobile Refinishing (1377402) file 6. NTIS

Study of the Catalytic Incineration of the Textile Stentor Gaseous Effluents (1374725) file 6. NTIS

Prevention or Control. Emissions and Costs of Emission Reduction of SO 2, NO X and Volatile Matter Until 2010, as Part of the National Energy Outlook 1987 (1365047) file 6. NTIS

Toxicology and Carcinogenesis Studies of Xylenes (Mixed) (60% m-Xylene, 14% p-Xylene, 9% o-Xylene, and 17% Ethylbenzene) (CAS No. 1330-20-7) in F344/N Rats and B6C3F1 Mice (Gavage Studies). (1256706) file 6. NTIS

Industrial Hygiene Walk-Through Survey Report of BASF Corporation - Inmont Division, Cincinnati, Ohio (1248919) file 6. NTIS

Health Hazard Evaluation Report HETA 85-188-1627, Distribution and Auto Service, Inc., Benecia, California (1196352) file 6. NTIS

Health Hazard Evaluation Report HETA 84-408-1522, U.S. Forest Service, Redding California (1138350) file 6. NTIS

Source Fingerprints for Receptor Modeling of Volatile Organics (90-00070) file 41. Pollution Abstracts

Waterborne Basecoat to Boost ICI Auto Business (86-01574) file 41. Pollution Abstracts

Urban Lead - A Study of Environmental Lead and Its Significance to School Children in the Vicinity of a Major Trunk Road (82-06188) file 41. Pollution Abstracts

A Comparison of Polymer Adsorbent and Bag Sampling Techniques for Paint Bake Oven Odorous Emissions (80-05715) file 41. Pollution Abstracts

Economic Aspects of Air Pollution and Its Control (78-03148) file 41. Pollution Abstracts

The State of Delaware Experience with EPA Reference Method 25 Audit Samples (0187130) (87-008047) file 40. Enviroline

Incentives for Technological Innovation in Air Pollution Reduction: An ETIP Policy Research Series. Internal Offsets and Technological Innovation: Six Case Studies (0164774) (83-003529) file 40. Enviroline

Acid Rain Vulnerability of the 27 States East of the Mississippi River (0155602) (82-001448) file 40. Enviroline

Environmental Effects of Increased Coal Utilization: Ecological Effects of Gaseous Emissions from Coal Combustion (0144935) (80-004802) file 40. Enviroline

The Urban Scene...Part I (0131163) (78-005851) file 40. Enviroline

Lead and Cadmium in Dusts and Soils in a Small Urban Community (0116045) (76-007086) file 40. Enviroline

Lead Content of Deciduous Teeth of Children in Different Environments (0112631) (76-003939) file 40. Enviroline

Air Quality Management in Los Angeles: Perspectives on Past and Future Emission Control Strategies (02770466) file 8. Compendex Plus

Porche's 10-Year No-Performance Guarantee (02755297) file 8. Compendex Plus

Morphology and Micro Structure of Electrodeposited Zinc-Iron Binary Alloy (02727164) file 8. Compendex Plus

Zinc-Manganese Alloy Electroplating on Steel Strip (02614709) file 8. Compendex Plus

New Technology for VOC Emission Control (02539950) file 8. Compendex Plus

Closed Loop Absorption for Solvent Recovery (02517706) file 8. Compendex Plus

Finishing the Job: Automotive-Wise (02513193) file 8. Compendex Plus

Source-Receptor Analysis of Volatile Hydro Carbons (02345549) file 8. Compendex Plus

Atmospheric Corrosion after 80 Years of Study (02319103) file 8. Compendex Plus

Recycling and Waste Air Purification on Spray Booths (02313600) file 8. Compendex Plus

High Solids Coatings: Are they Cost Effective? (02253805) file 8. Compendex Plus

Production of Fe-Zn Alloy Electroplating Sheet Steel by New Horizontal Electrolytic Cell: Development of Manufacture Technology for Fe-Zn Alloy Electroplation Sheet Steel (02217897) file 8. Compendex Plus

Evaluation of Low VOC Chassis Paint (02154149) file 8. Compendex Plus

Fluidized Bed Paint Stripping and Sludge Burning (02132419) file 8. Compendex Plus

Finishing '85: Conference Proceedings (02124237) file 8. Compendex Plus

Zinc-Manganese Alloy Electroplated Steel for Automotive Body (02110668) file 8. Compendex Plus

KPR System for VOC Emission Control from Paint Spray Booths (02072539) file 8. Compendex Plus

Fly Ash Emissions from a Power Plant and Damage to Automobile Finishes (02022994) file 8. Compendex Plus

ICI Wins Pollution Abatement Award for Low Solvent Emission Paints (02018553) file 8. Compendex Plus

Corrosion Resistance and Paintability of Zn-Mn Alloy Plated Steel Sheets (02017036) file 8. Compendex Plus

Source Discrimination of Short-Term Hydrocarbon Samples Measured Aloft (01987495) file 8. Compendex Plus

Low VOC Coatings for Automotive Plastics (01883996) file 8. Compendex Plus

Working Out and Investigation of Car's Protective Coatings of Petroleum Base (01636818) file 8. Compendex Plus

Automotive Trim Corrosion: Causes and Effects (01598936) file 8. Compendex Plus

Energy, Environmental, and Safety Benefits Through Computer Controlled Curing Oven Processes (01449658) file 8. Complex Plus

Recent Progress of Acrylic Emulsion for Coating Industries (01410669) file 8. Compendex Plus

Controlling Fugitive VOC Emissions From the Metal Finishing Industry (01336938) file 8. Compendex Plus

Application of Target Transformation Factor Analysis to Aerosol Source Resolution (01257731) file 8. Compendex Plus

Automotive Paint System Hydrocarbon Control at a Practical Cost (01078017) file 8. Compendex Plus

Automotive Challenges to the Finishing Industry (00958928) file 8. Compendex Plus

Ambient Hydrocarbon and Ozone Measurements Downwind of a Large Automotive Painting Plant (00934510) file 8. Compendex Plus

Design and Development of Small Internal Combustion Engines, 1978 (00876396) file 8. Compendex Plus

Technical Papers: Second Chemical Coatings Conference's Electrocoating Session, High Solids Coatings Session, Power Coatings Session, Radiation Cured Coatings Session, Water-Borne Coatings Session, 1978 (00875478) file 8. Compendex Plus

State Air Quality Plan and the Modernization of Automotive Painting Facilities (00847852) file 8. Compendex Plus

Proceedings of the Ninth Annual Environmental Systems Symposium, 1987 (00816683) file 8. Compendex Plus

Proceedings of the Fifth Water-Borne and Higher Solids Coatings Symposium, 1978 (00802050) file 8. Compendex Plus

Control of Volatile Organic Emissions from Existing Stationary Sources, Volume II: Surface Coatings of Miscellaneous Metal Parts and Products (00794280) file 8. Compendex Plus

Materials and Coating and Coatings for Thermal Reactors to Control Automotive Emissions (00722746) file 8. Compendex Plus *Italian*

Rapid Weathering of Wood and Paintings Under the Additional Influence of Sulphur Dioxide (00660208) file 8. Compendex Plus *German*

Reducing Solvent Emissions in Automotive Spray Painting (00565542) file 8. Compendex Plus

Tracer Studies of Ingestion of Dust by Urban Children (00559826) file 8. Compendex Plus

A Practical Application of EDM to Manufacture Repeatable Burr Free Metering Orifices in Carburetor Components (00396775) file 8. Compendex Plus

Evaluation of Alloys and Coatings for Use in Automobile Thermal Reactors (00367398) file 8. Compendex Plus

Active Aluminas as Catalyst Supports for Treatment of Automotive Exhaust Emissions (00297955) file 8. Compendex Plus

Seven Incinerators Control Paint Oven Emissions (00226024) file 8. Compendex Plus

First High-Volume Epoxy Powder Coating Line in Auto Industry (00219922) file 8. Compendex Plus

Electrocuring Accelerates Production at Ford (00197816) file 8. Compendex Plus

APPENDIX 2

(Data Analyses)

Quantitative Analyses of Laboratory and Field Test Data

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(1) Numerical Damage Ratings

During the program, it became evident that quantitative evaluations were needed to properly discern test relationships. In visual analyses of coatings, statistical methods should be employed to ascertain the validity of the results and mitigate the subjective aspects of the rating process. A simple procedure was developed to quantify the visual inspection results.

The performance of the wax/paint system in resisting acid rain damage was quantified in terms of a Paint Damage Factor. Specimens determined to be damage free by both inspection personnel (ND) were given a numerical rating of 0.0. In cases where the inspectors disagreed on whether the specimens were damaged (PD), the specimens were given a numerical rating of 0.5. Specimens judged to be damaged by both inspectors (D) were given a numerical rating of 1.0. Test results were readily quantified and the data for each set of tests were entered on a spread sheet. Graphs were made of the quantified Paint Damage Factors plotted against specific test parameters.

(2) Graph Interpolations

All graph interpolations were done using a Power Regression Model with the exception of Figures 4 and 5 which were fitted with a Linear Regression Model and Figure 26 which was fitted with a Parabolic Regression Model. The different interpolations were due to the nature of the data trends. The success of an analytical exercise depends on the proper choice of quantitative criteria, which determine the quality of the fitted model. The Coefficient of Determination, r^2, is the measure of the fit of the regression line. It represents the proportion of variation in the Response Data that is explained by the model.

Parabolic Model

$$y=a+bX+cX^2$$

Coefficients

$$a=\frac{1}{n}\left(\sum y_i-c\sum X_I^2-b\sum X_I\right)$$

$$b=\frac{\left[n\sum X_iY_i-\left(\sum X_i\right)\left(\sum Y_i\right)\right]-c\left[n\sum X_i^3-\left(\sum X_i\right)\left(\sum i^2\right)\right]}{n\sum X_i^2-\left(\sum X_i\right)^2}$$

$$c=\frac{A-B}{[n\sum X_i^2-(\sum X_i)^2][n\sum X_i^4-(\sum X_i^2)^2]-[n\sum X_i^3-(\sum X_i)(\sum X_i^2)]^2}$$

Where

$$A=[n\sum X_i^2-(\sum X_i)^2][n$$

$$B=[n\sum X_i^3-(\sum X_i)(\sum X_i^2)][n\sum X_iY_i-(\sum X_i)(\sum Y_i)]$$

$$r^2=\frac{a\sum Y_i+b\sum X_iY_i+c\sum X_i^2Y_i-\frac{(\sum Y_i)^2}{n}}{\sum Y_i^2-\frac{(\sum Y_i)^2}{n}}$$

Power Model

$$y=aX^b$$

Coefficients

$$a=\exp[\frac{\sum \ln Y_i}{n}-b\frac{\sum \ln X_i}{n}]$$

$$b=\frac{\sum(\ln X_i)(\ln Y_i)-\frac{(\sum \ln X_i)(\sum \ln Y_i)}{n}}{\sum(\ln X_i)^2-\frac{(\sum X_i)^2}{n}}$$

$$r^2=\frac{\left[\sum \ln Y_i \ln X_i - \frac{\sum \ln X_i \sum \ln Y_i}{n}\right]}{\left[\sum (\ln X_i)^2 - \frac{(\sum \ln X_i)^2}{n}\right]\left[\sum (\ln Y_i)^2 - \frac{(\sum \ln Y_i)^2}{n}\right]}$$

Linear Model

$$y=a+bX$$

Coefficients

$$a=\frac{\sum Y_i}{n}-b\left[\frac{\sum X_i}{n}\right]$$

$$b=\frac{\sum X_i Y_i - \frac{\sum X_i \sum Y_i}{n}}{\sum X_i^2 - \frac{(\sum X_i)^2}{n}}$$

$$r^2=\frac{\left[\sum X_i Y_i - \frac{\sum X_i \sum Y_i}{n}\right]^2}{\left[\sum X_i^2 - \frac{(\sum X_i)^2}{n}\right]\left[\sum Y_i^2 - \frac{(\sum Y_i)^2}{n}\right]}$$

(3) Graphs

The resulting graphs follow. Where comparisons are provided, log-log plots are used to represent the data. Each graph also includes the r^2 values to indicate the degree of fit for each data set. Figure 1 shows the typical data dispersion and fit for a log-log plot with an r^2 value of 0.78. To clarify the other graphs, individual data points have been omitted.

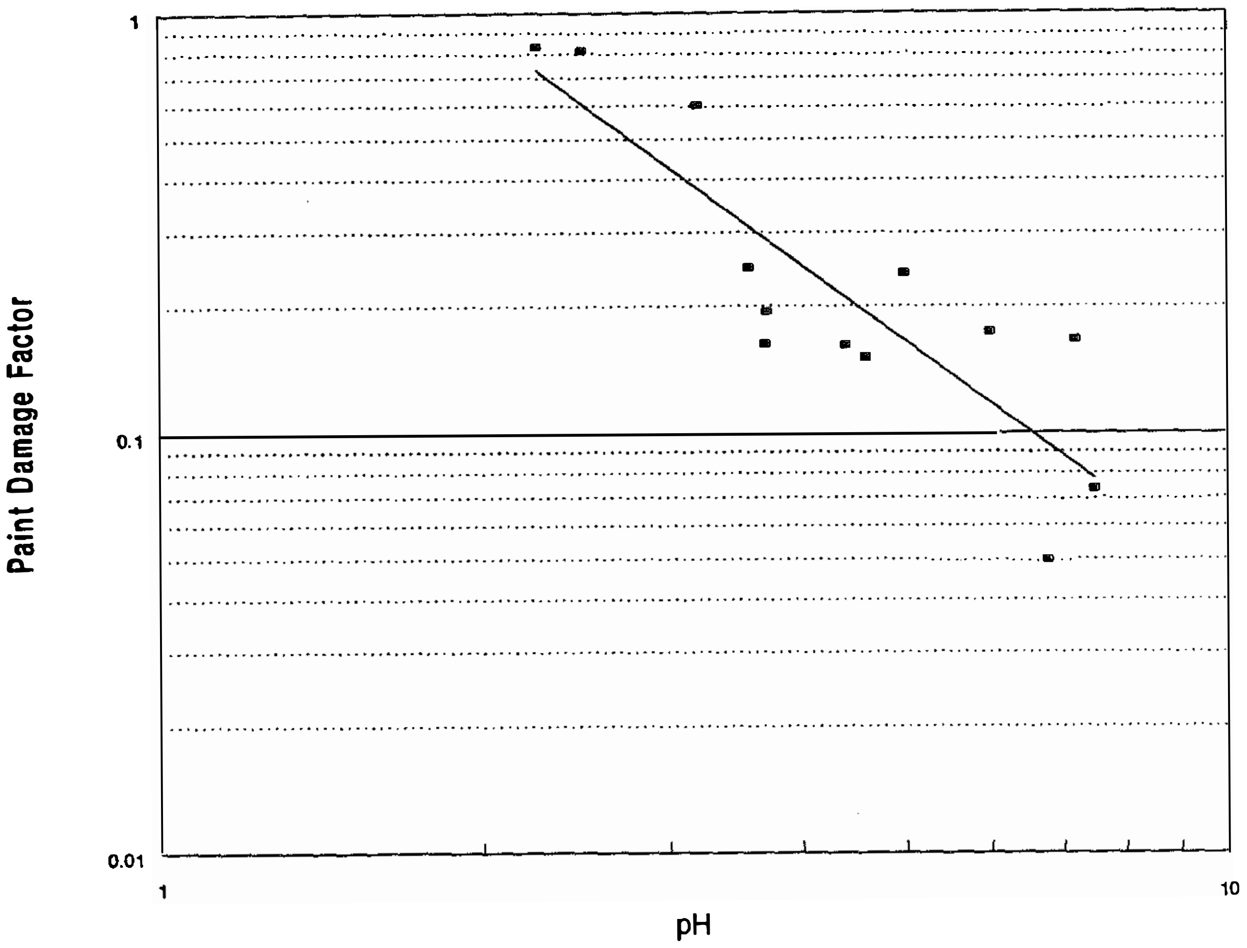


Figure 1. Plot of Paint Damage Factor vs pH Averaged for All Tests - Light Blue Paint (r^2=0.78).

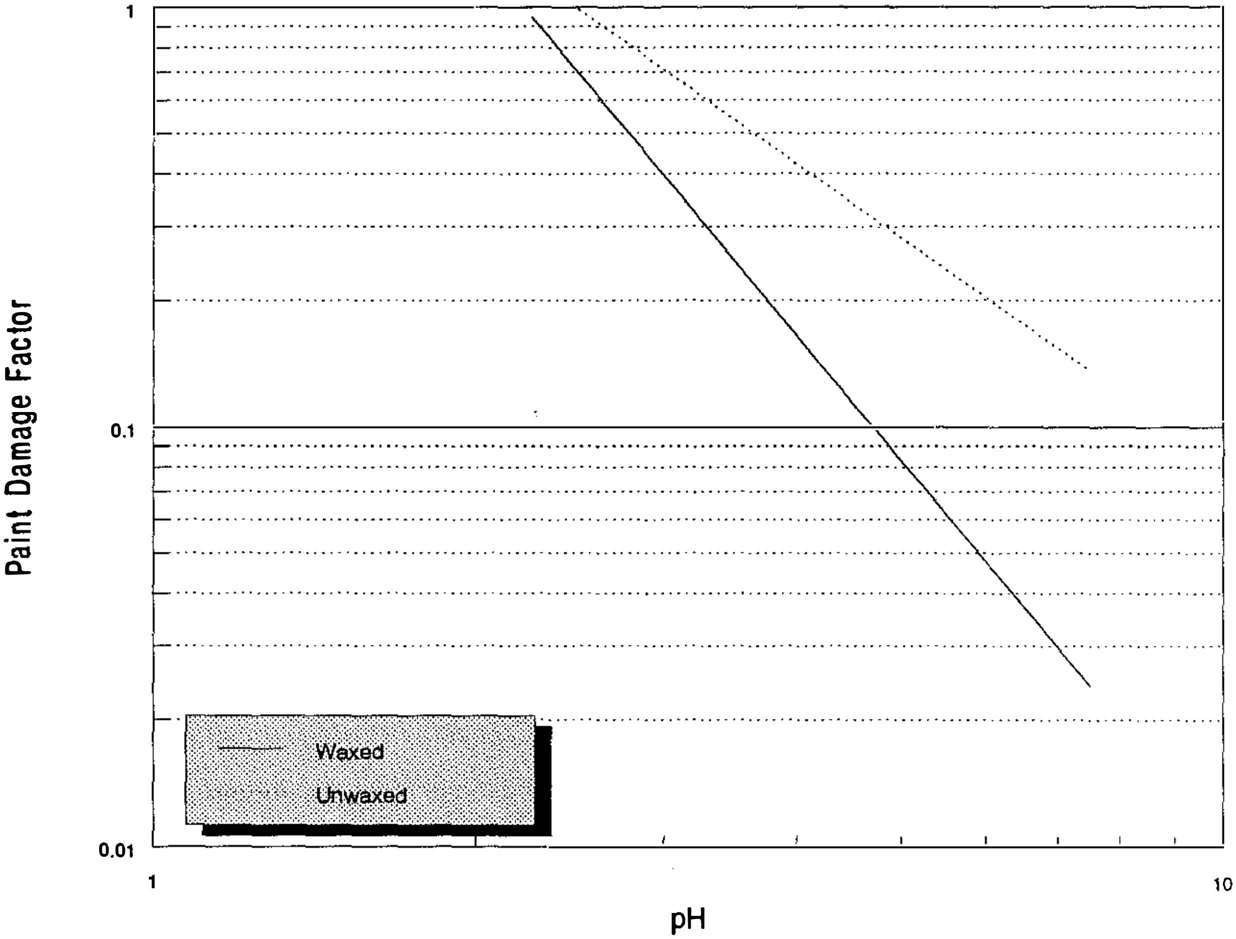


Figure 2. Plot of Paint Damage Factor vs pH for Cyclic Evaporation Tests, All Data - Waxed (r^2=0.85) and Unwaxed (r^2=0.76).

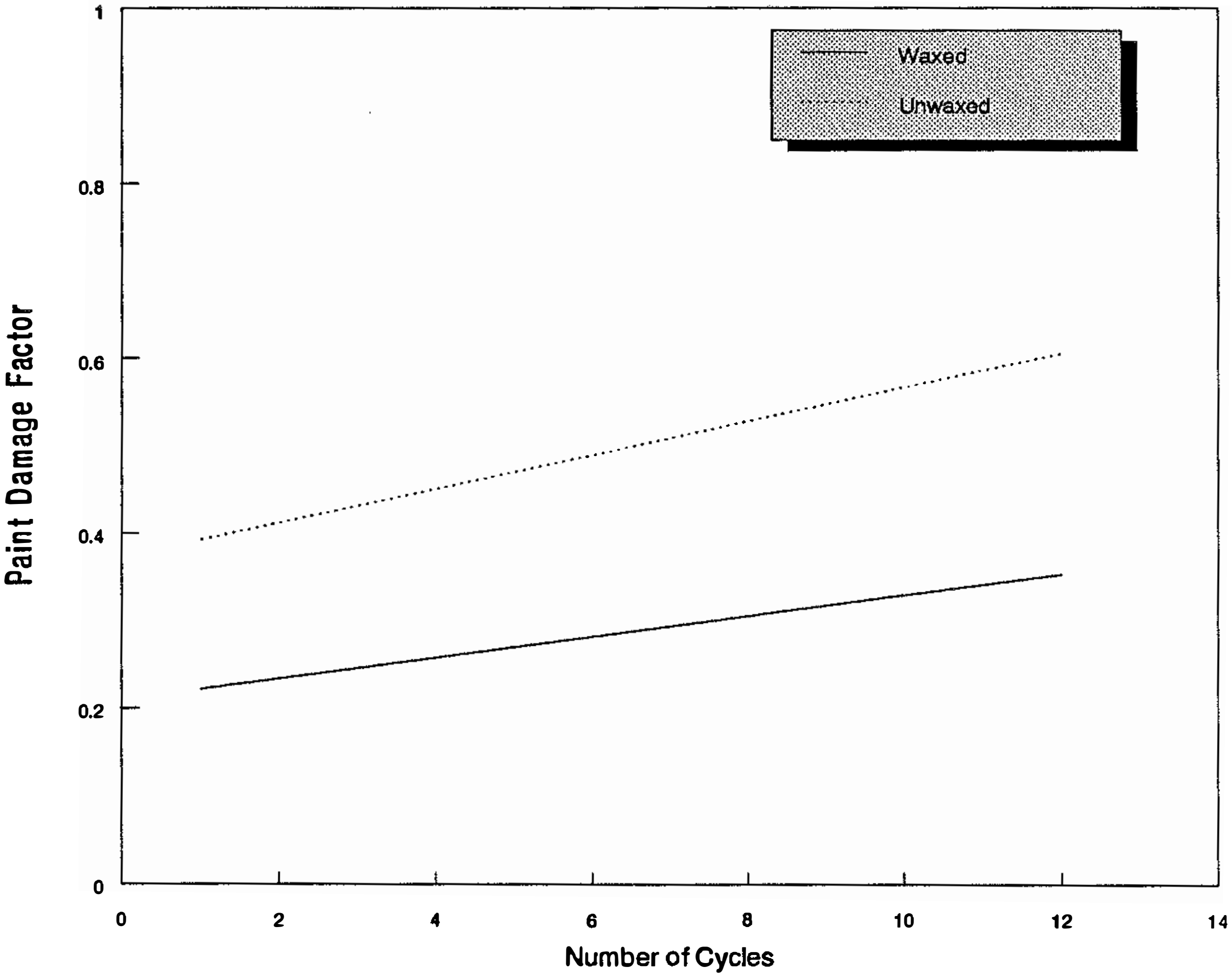


Figure 3. Plot of Paint Damage Factor vs Number of Evaporation Cycles for Cyclic Evaporation Tests, All Data - Waxed (r^2=0.84) and Unwaxed (r^2=0.84).

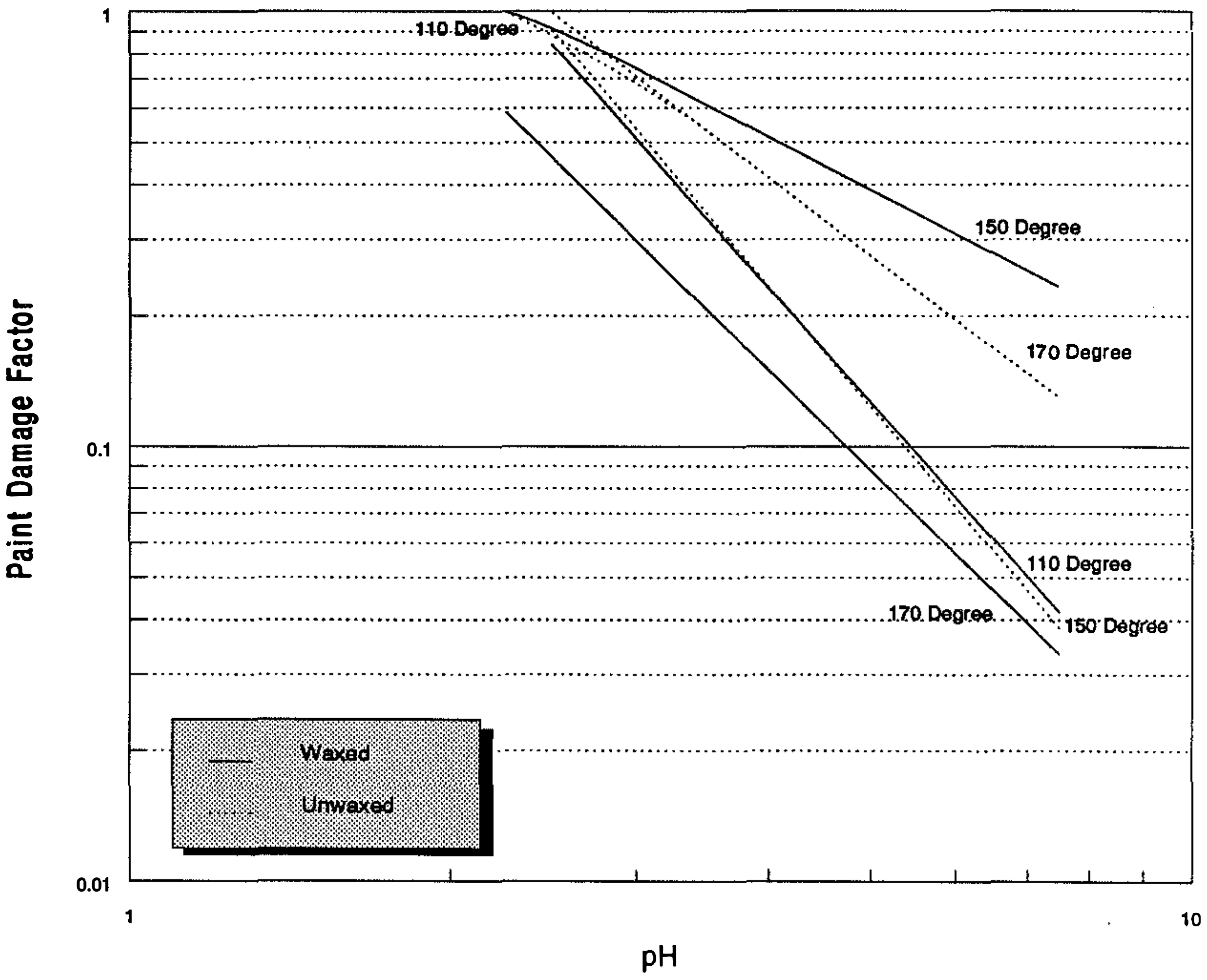


Figure 4. Plot of Paint Damage Factor vs pH for all Cyclic Evaporation Test Data - Waxed - 110 °F (r^2=0.74), 150 °F (r^2=0.92), 170 °F (r^2=0.73); and Unwaxed - 110 °F (r^2=0.74), 150 °F (r^2=0.67), 170 °F (r^2=0.76). (Note that the plots for the Unwaxed Data at 110 and 170 °F are Practically Identical for Much of the Test Range.)

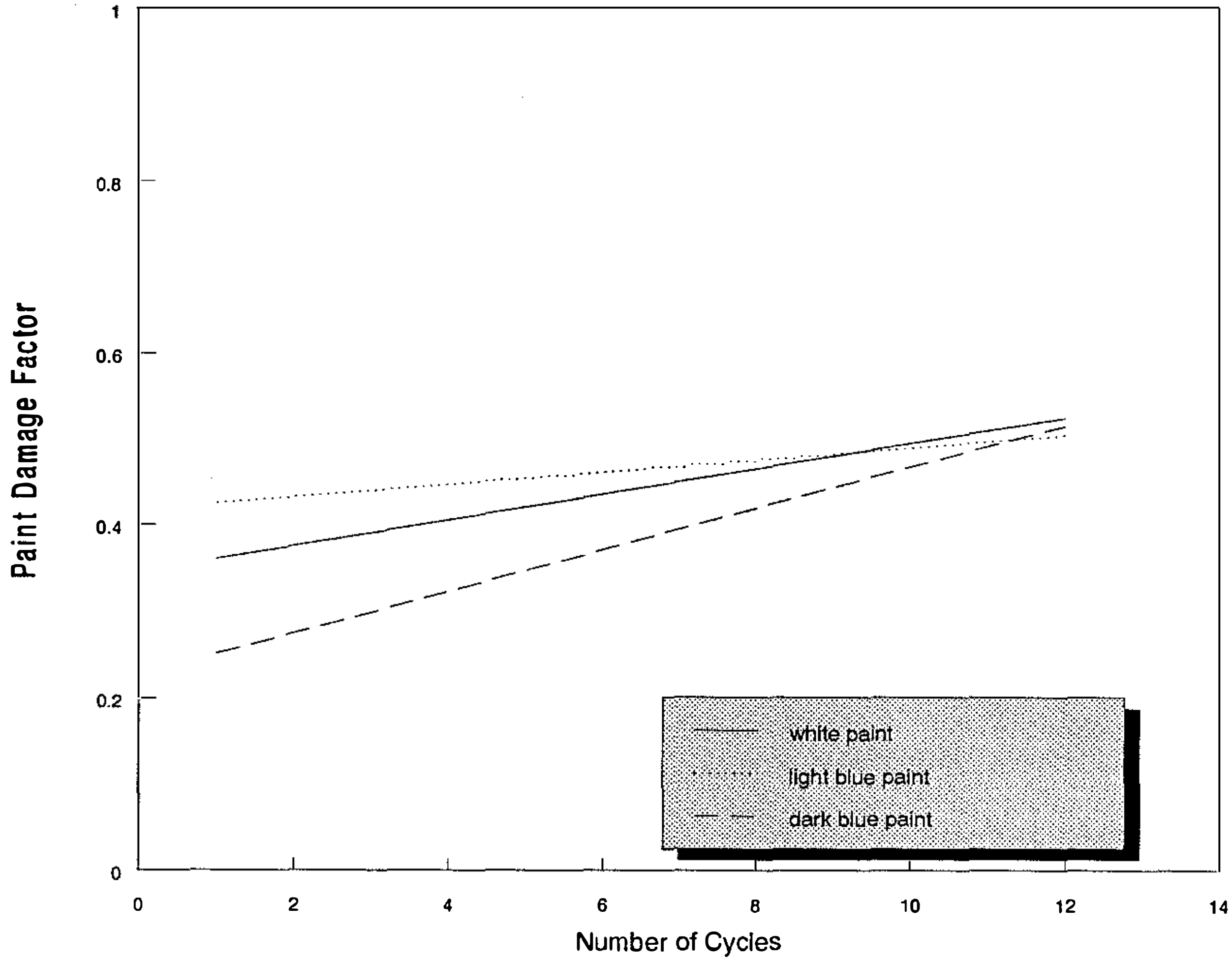


Figure 5. Plot of Paint Damage Factor vs Number of Evaporation Cycles for All Cyclic Evaporation Data - White ($r^2=0.79$), Light Blue ($r^2=0.75$), and Dark Blue ($r^2=0.63$).

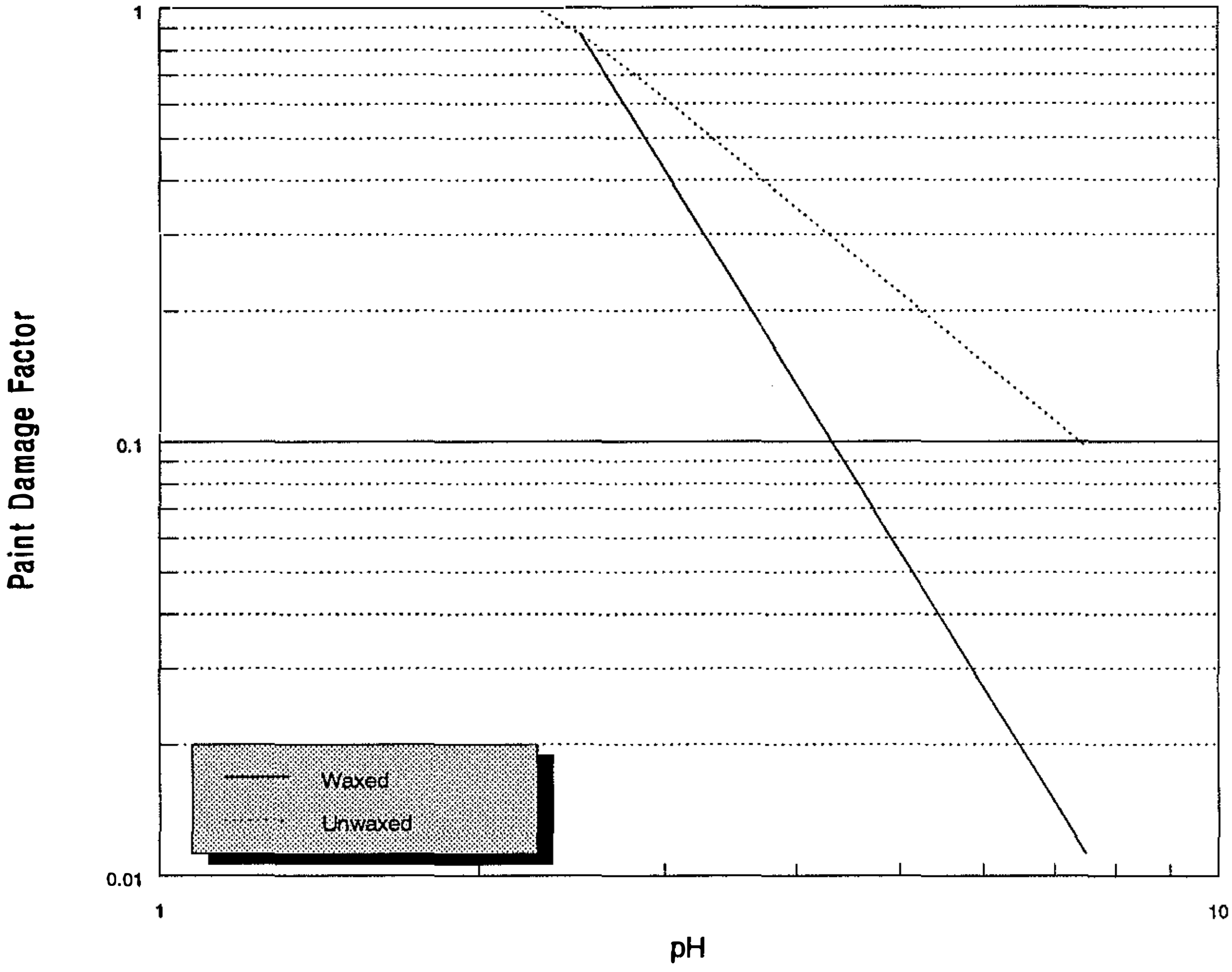


Figure 6. Plot of Paint Damage Factor vs pH for All Cyclic Evaporation Tests Using White Paint - Waxed (r^2=0.72) and Unwaxed (r^2=0.78).

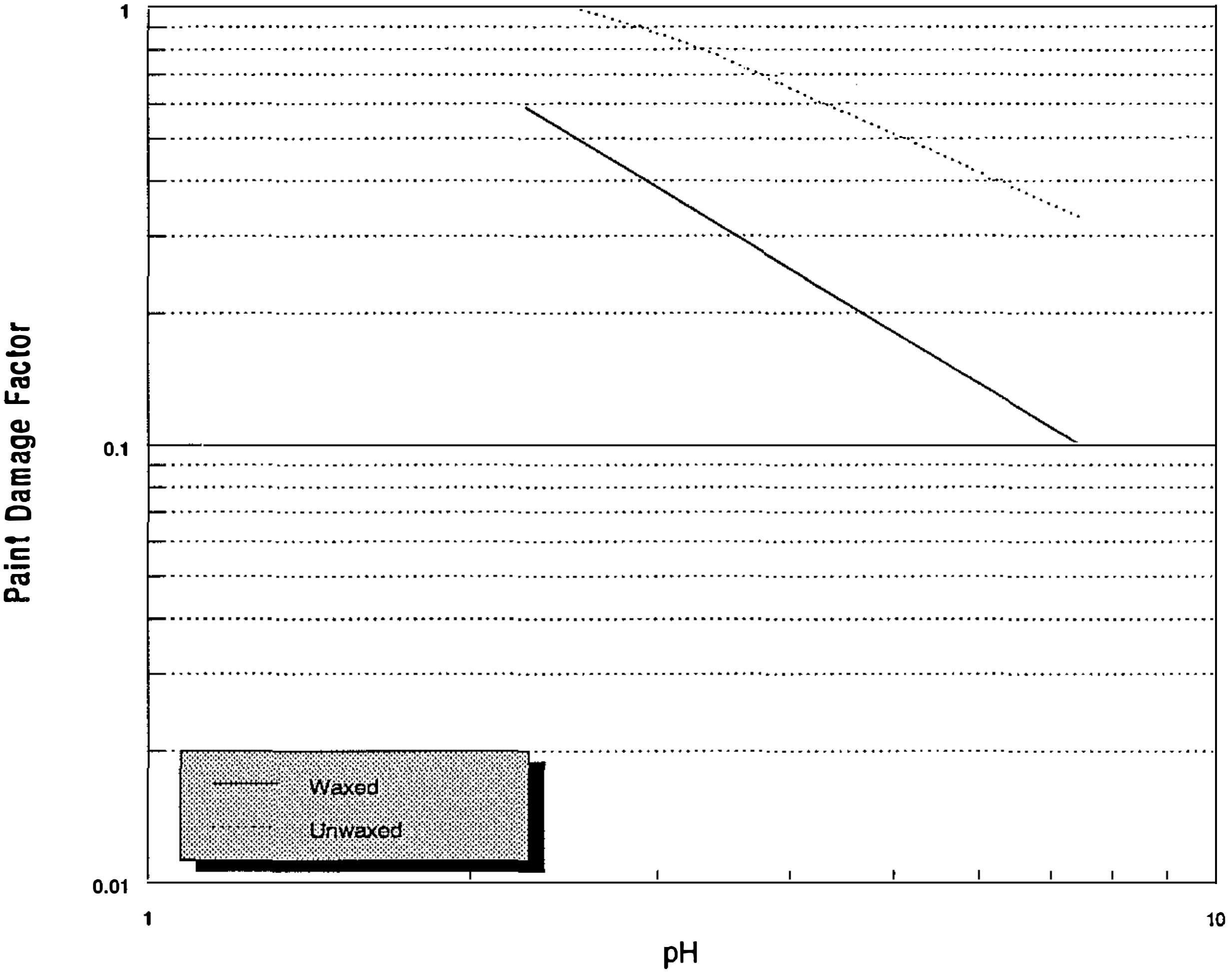


Figure 7. Plot of Paint Damage Factor vs pH for All Cyclic Evaporation Tests Using Light Blue Paint - Waxed (r^2=0.43) and Unwaxed (r^2=0.50).

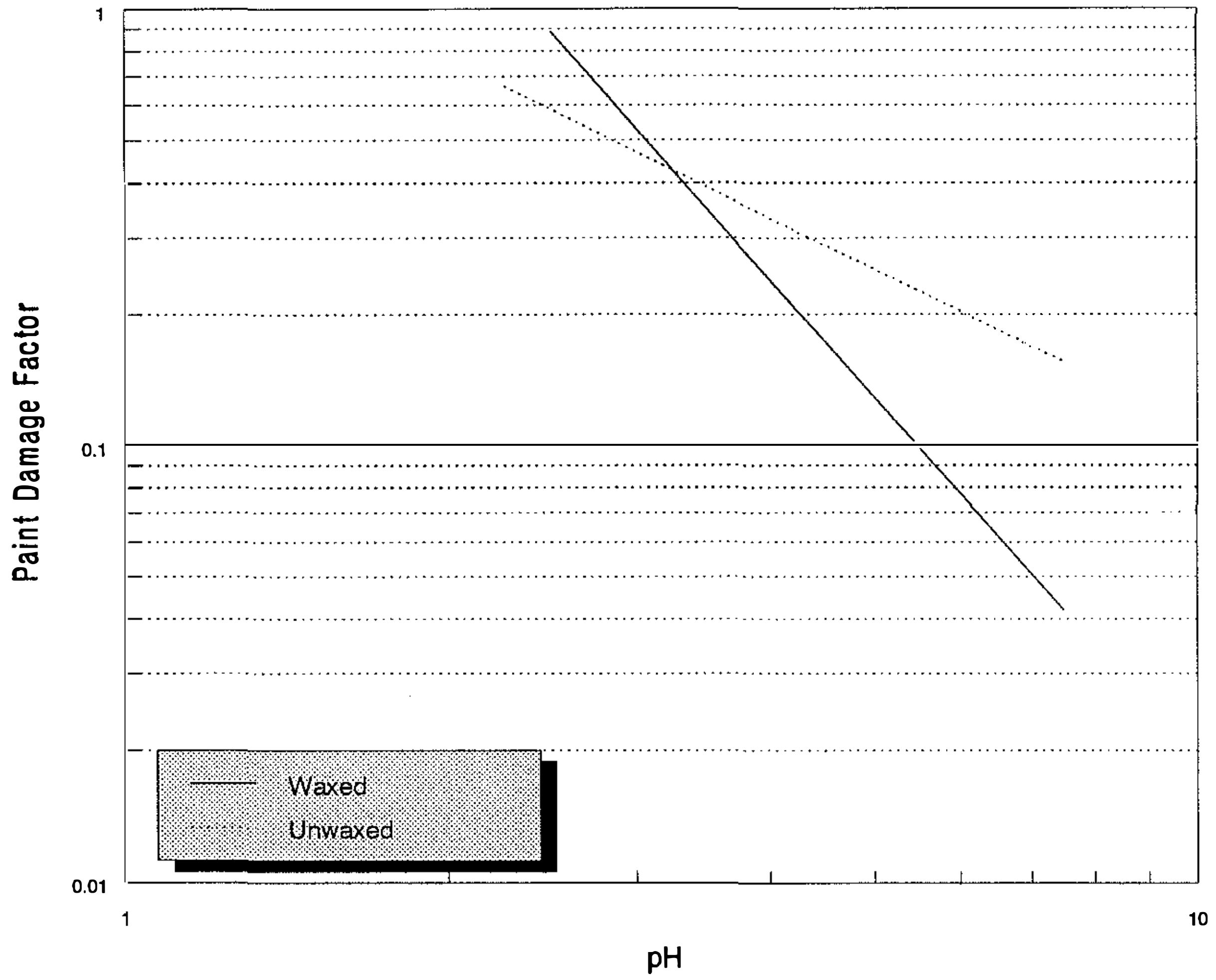


Figure 8. Plot of Paint Damage Factor vs pH for All Cyclic Evaporation Tests Using Dark Blue Paint - Waxed (r^2=0.91) and Unwaxed (r^2=0.42).

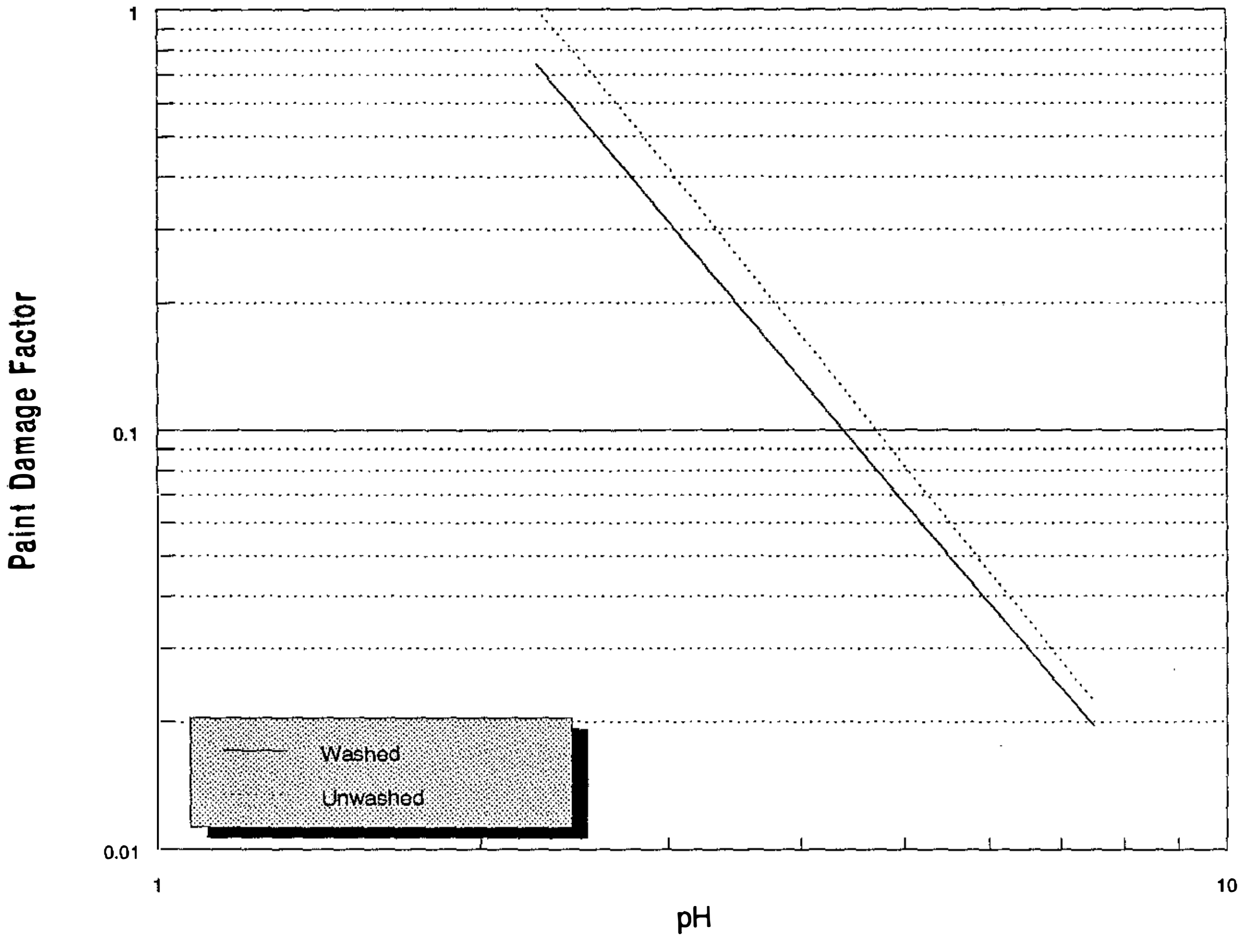


Figure 9. Plot of Paint Damage Factor vs pH for All Soak Tests - Washed (r^2=0.77) and Unwashed (r^2=0.87).

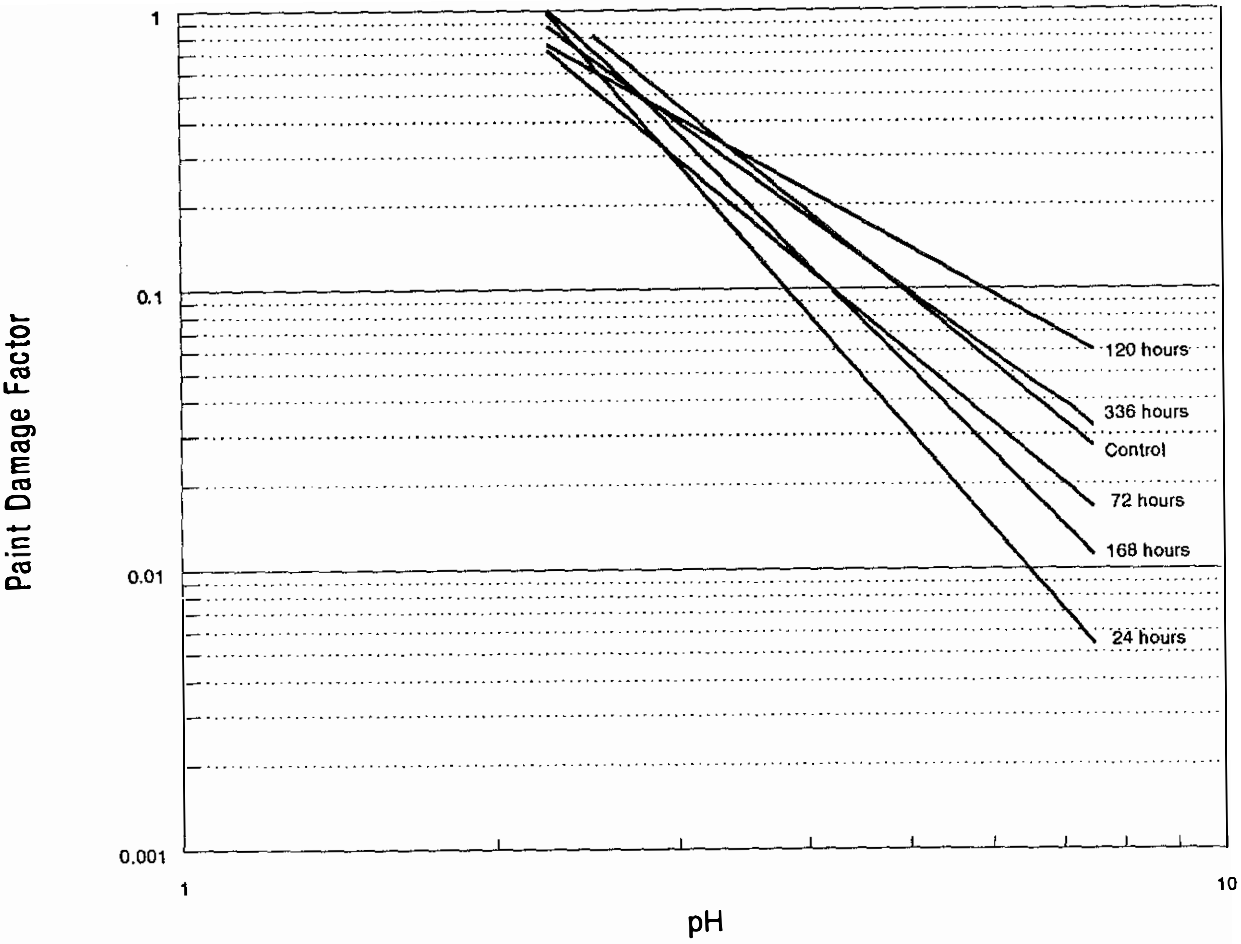


Figure 10. Plot of Paint Damage Factor vs pH for All Soak Tests, Washed and Unwashed, Showing the Effect of Soaking Time - Control (r^2=0.97), 24-Hour Soak (r^2=0.81), 72-Hour Soak (r^2=0.59), 120-Hour Soak (r^2=0.65), 168-Hour Soak (r^2=0.78), and 336-Hour Soak (r^2=0.74).

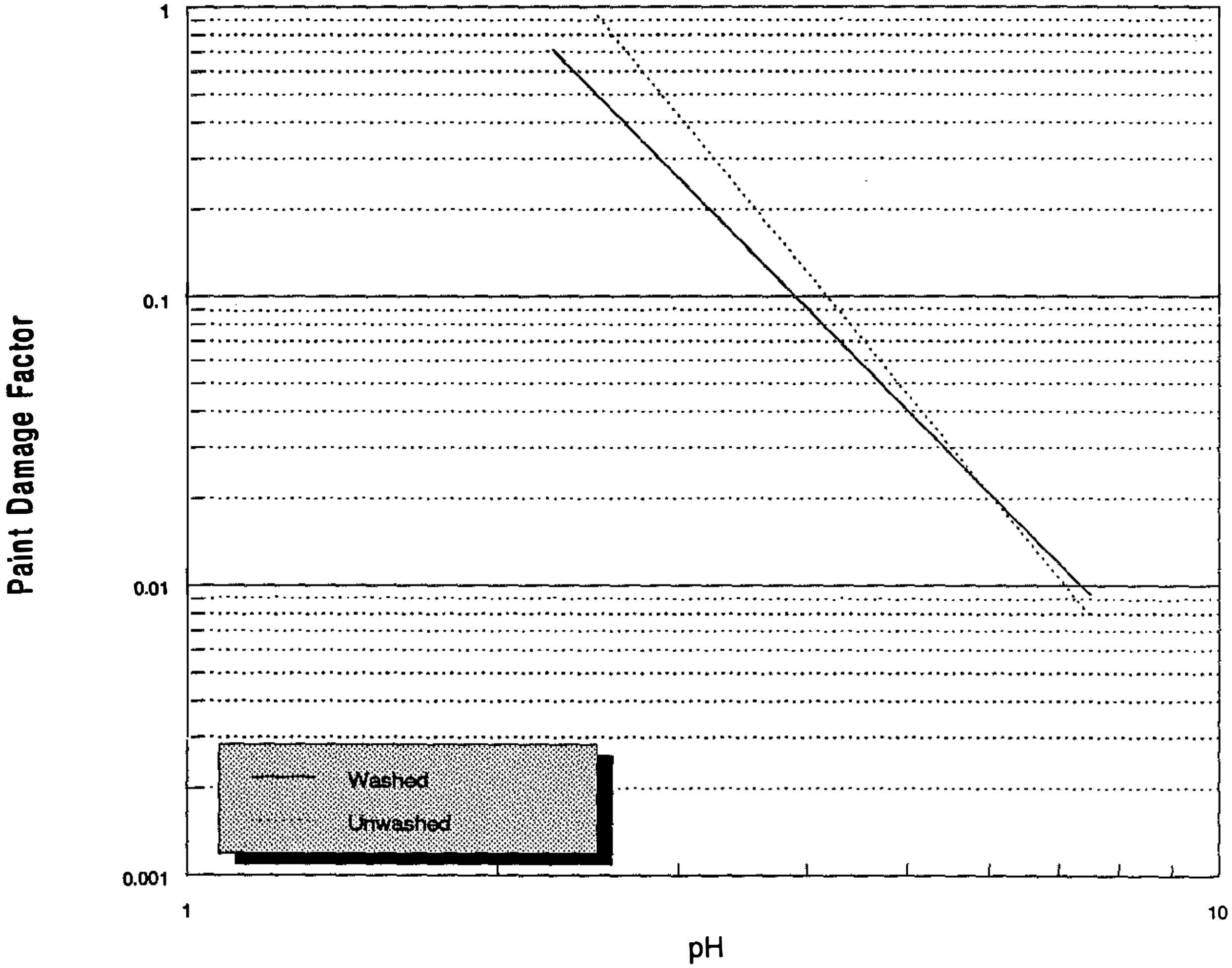


Figure 11. Plot of Paint Damage Factor vs pH for All 24-Hour Soak Tests - Washed (r^2=0.63) and Unwashed (r^2=0.94).

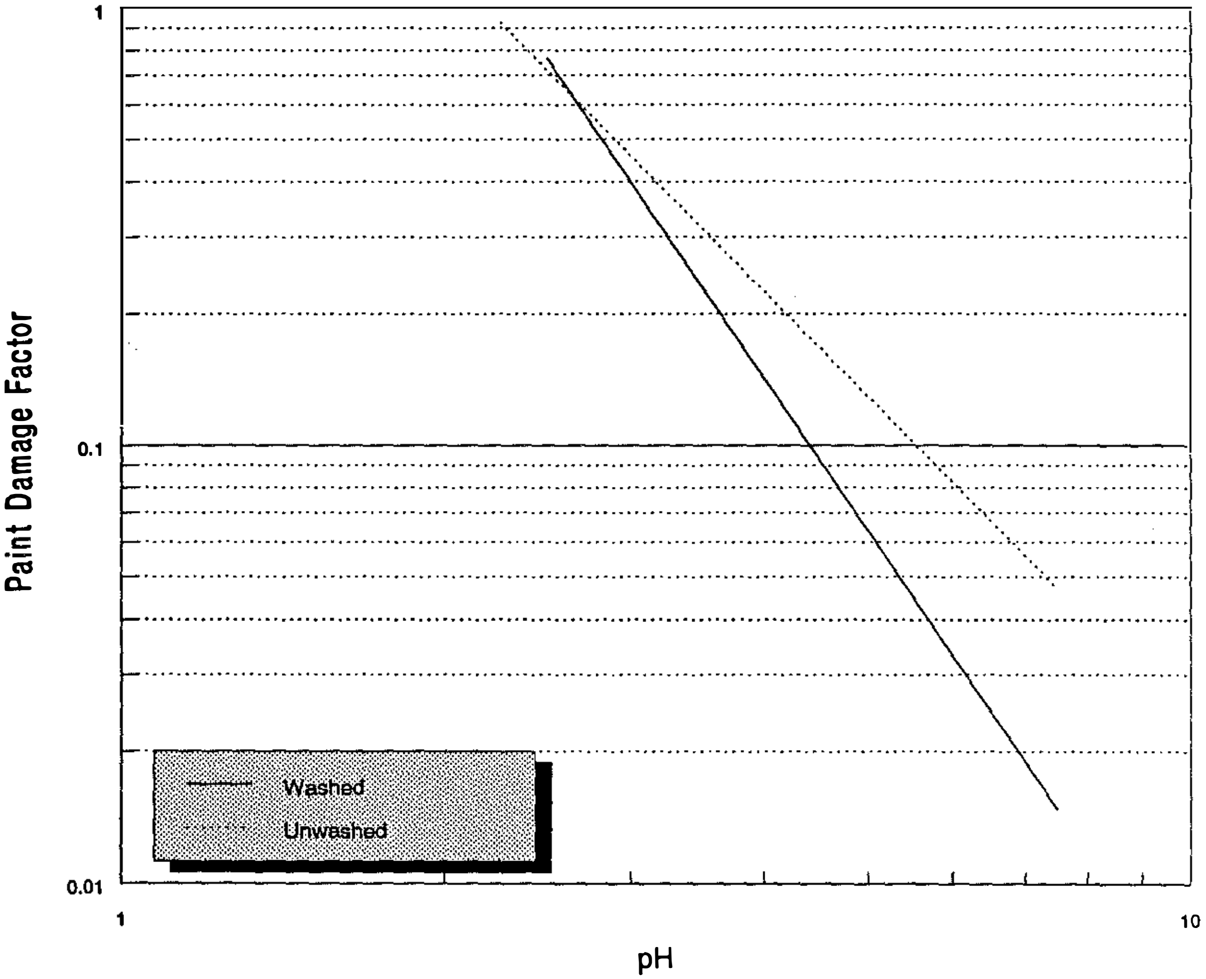


Figure 12. Plot of Paint Damage Factor vs pH for All 72-Hour Soak Tests - Washed (r^2=0.86) and Unwashed (r^2=0.63).

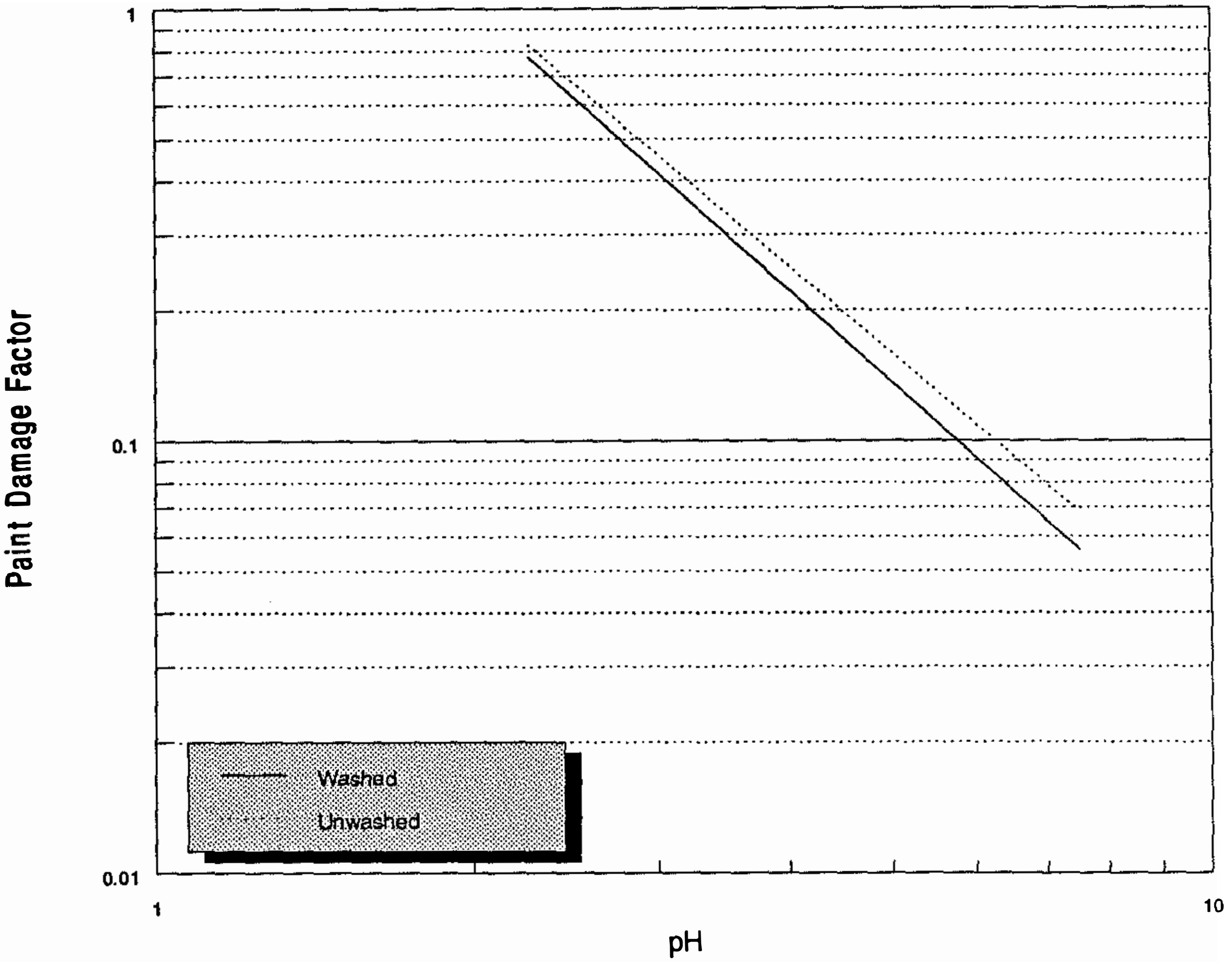


Figure 13. Plot of Paint Damage Factor vs pH for All 120-Hour Soak Tests - Washed (r^2=0.75) and Unwashed (r^2=0.66).

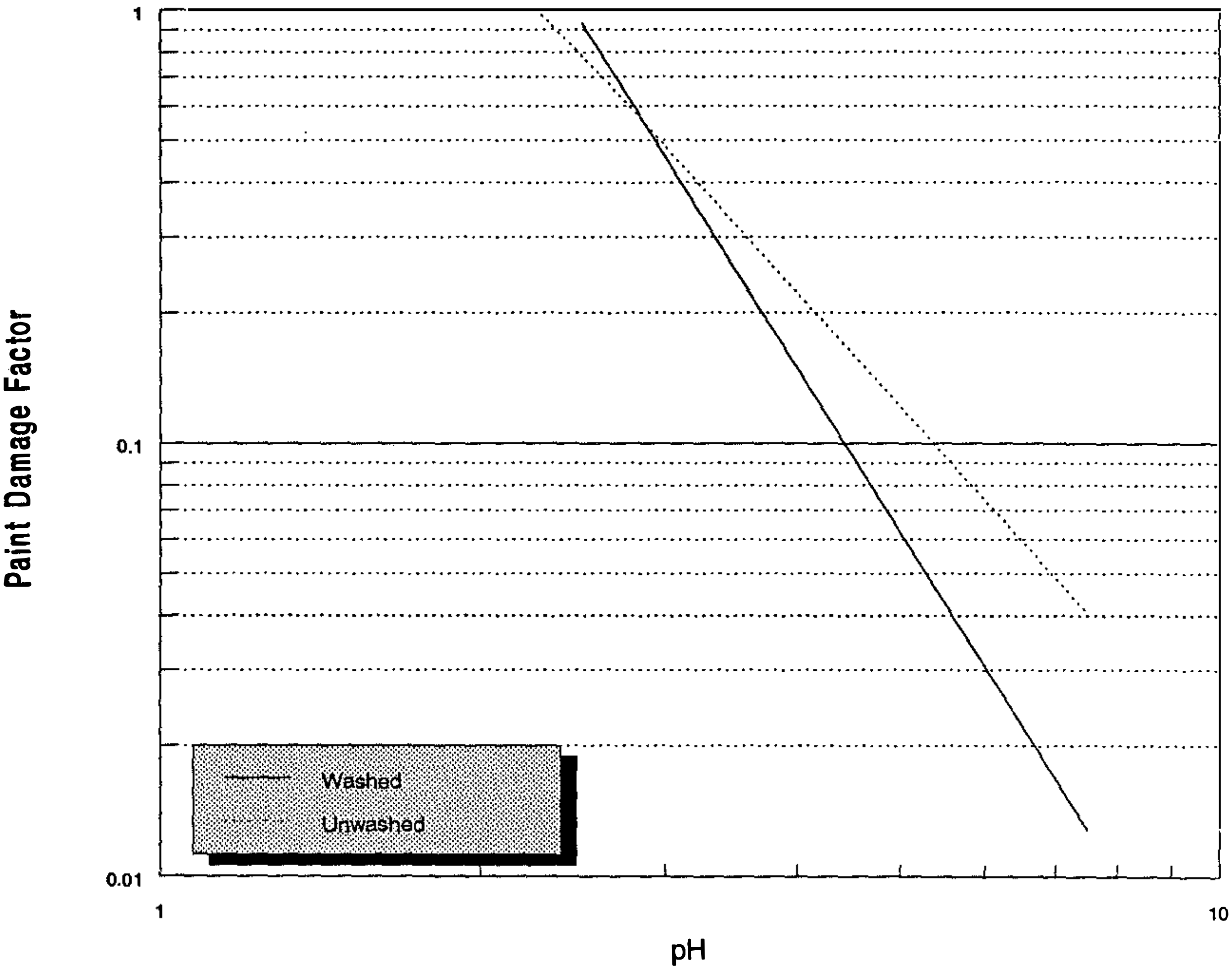


Figure 14. Plot of Paint Damage Factor vs pH for All 168-Hour Soak Tests - Washed (r^2=0.87) and Unwashed (r^2=0.78).

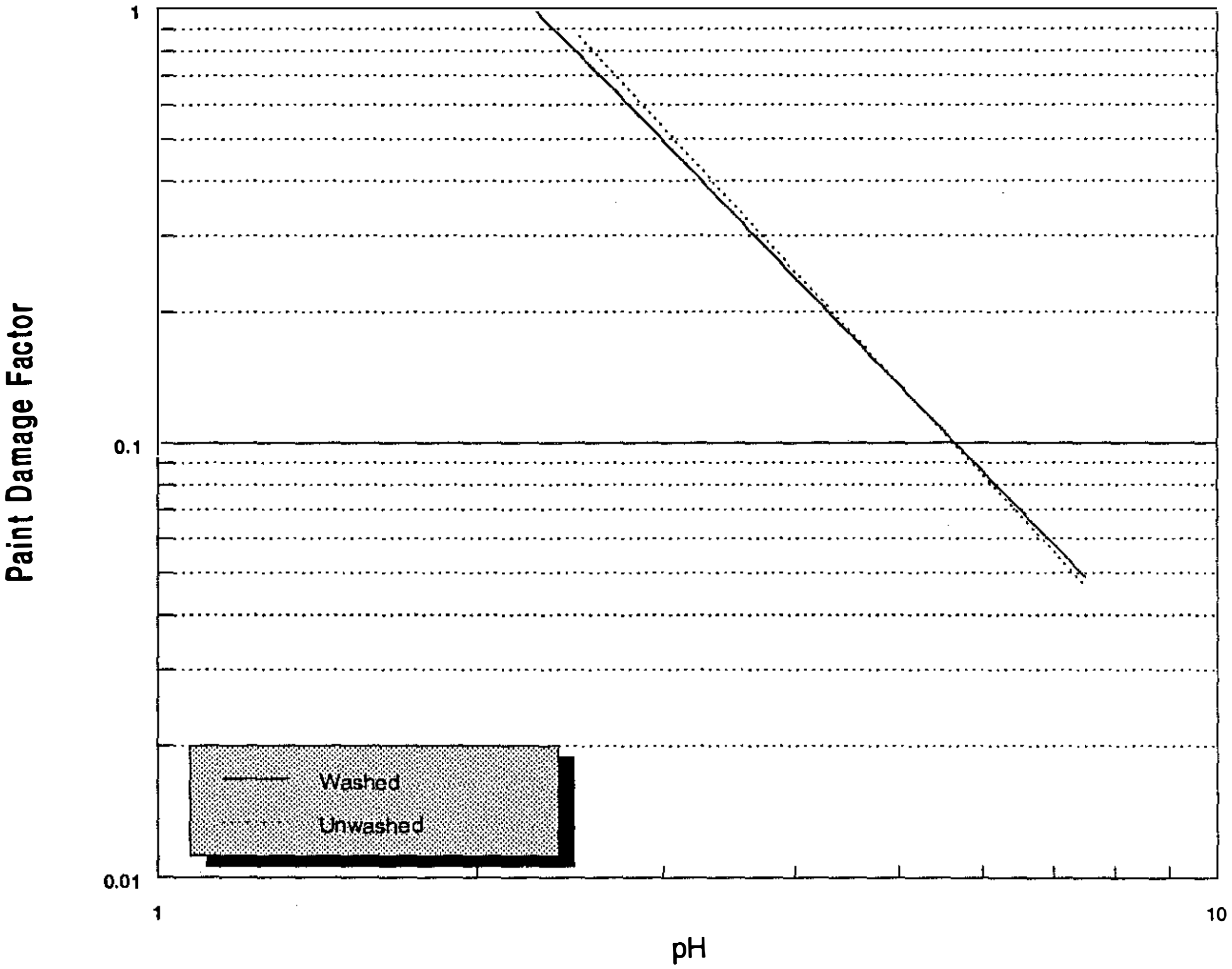


Figure 15. Plot of Paint Damage Factor vs pH for All 336-Hour Soak Tests - Washed (r^2=0.92) and Unwashed (r^2=0.86).

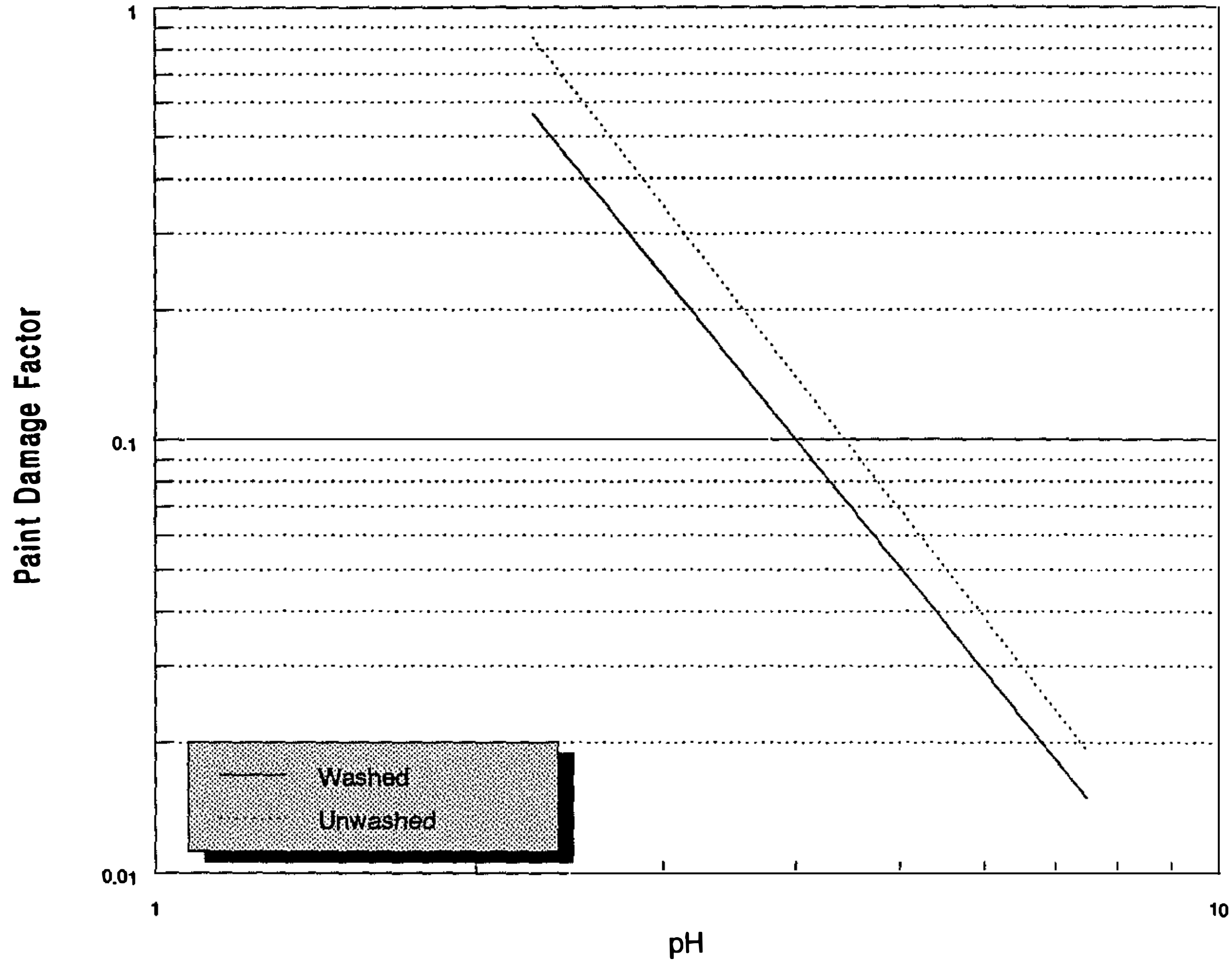


Figure 16. Plot of Paint Damage Factor vs pH for All Soak Tests Using White Paint - Washed (r^2=0.59) and Unwashed (r^2=0.73).

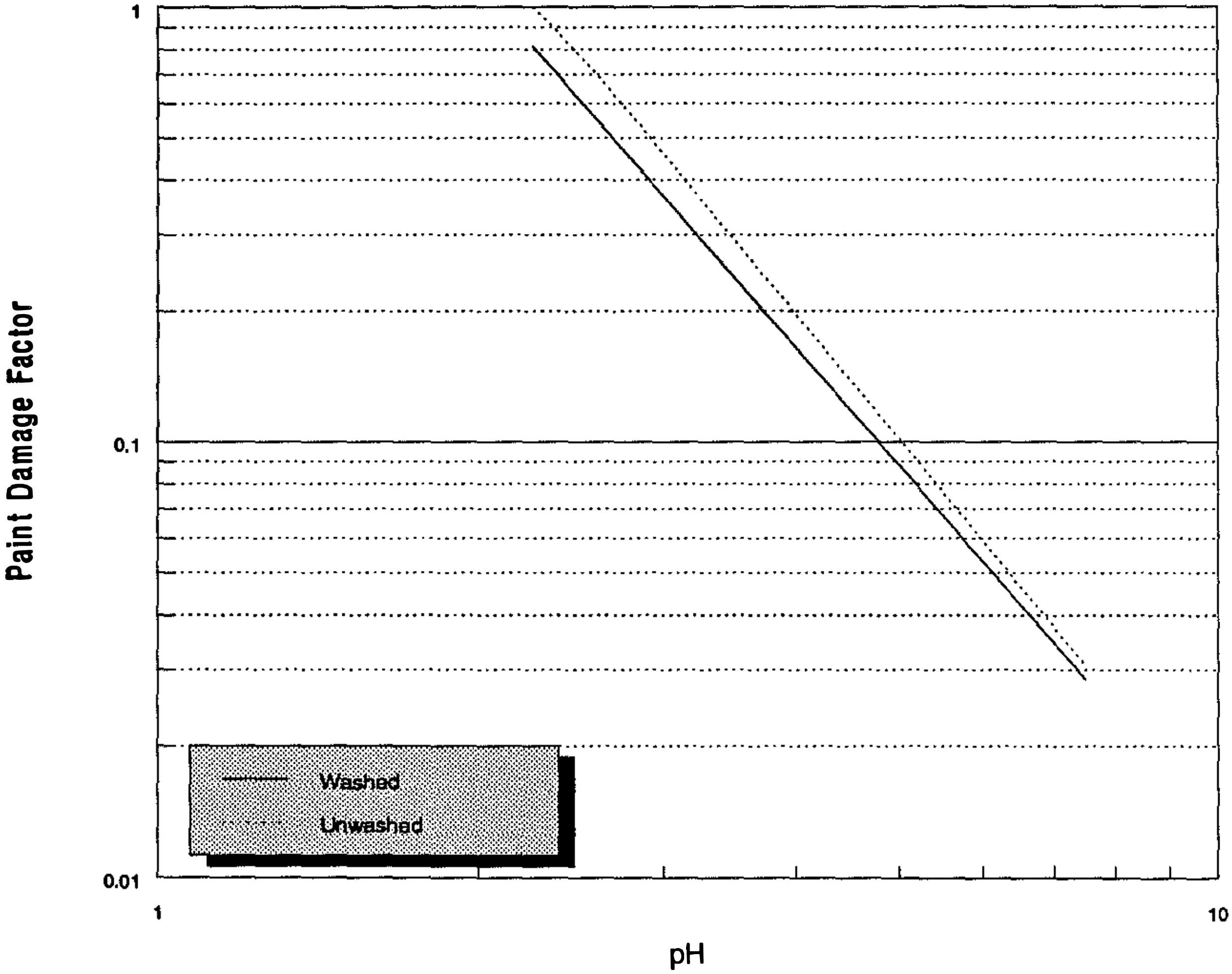


Figure 17. Plot of Paint Damage Factor vs pH for All Soak Tests Using Light Blue Paint - Washed (r^2=0.72) and Unwashed (r^2=0.83).

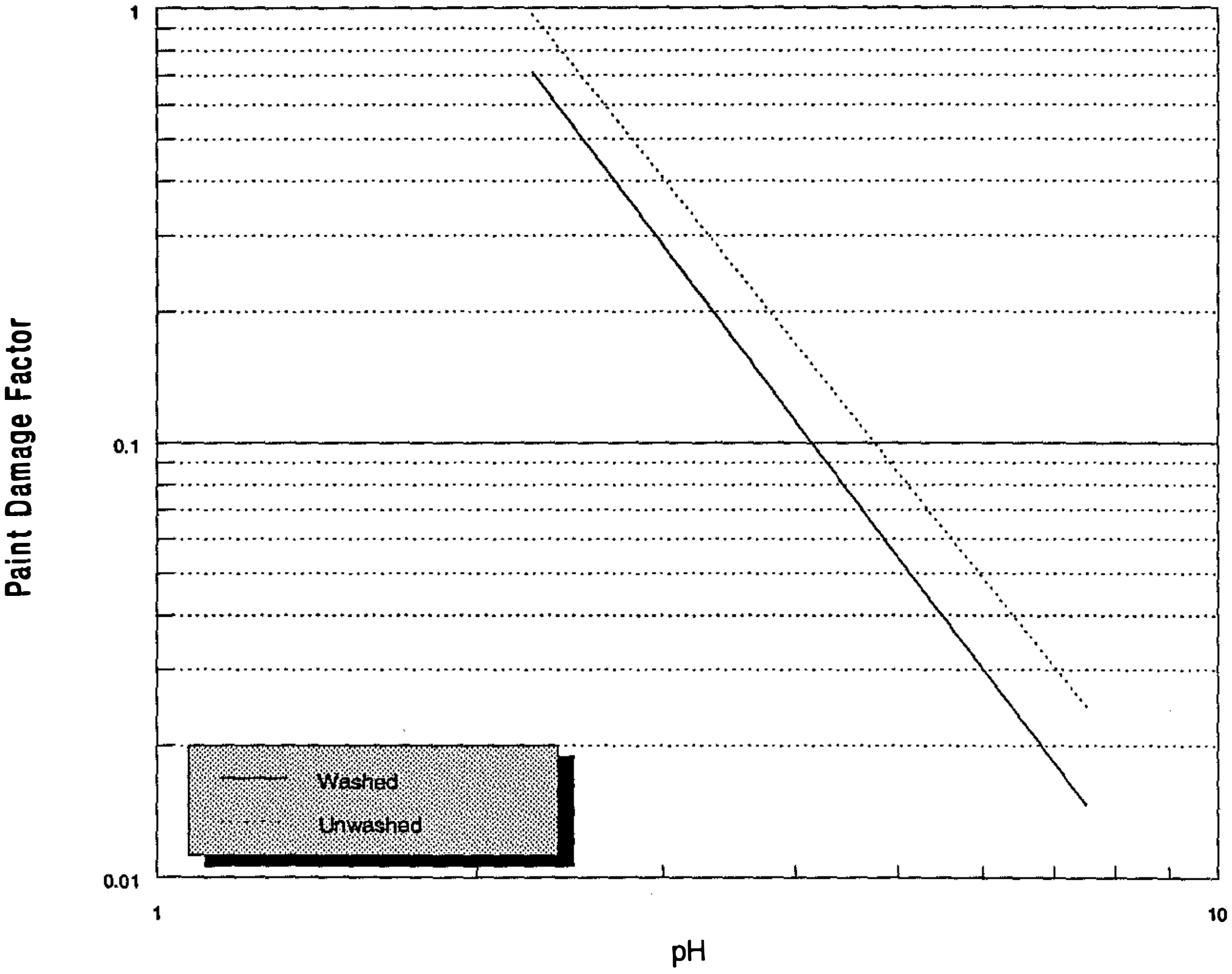


Figure 18. Plot of Paint Damage Factor vs pH for All Soak Tests Using Dark Blue Paint - Washed (r^2=0.67) and Unwashed (r^2=0.76).

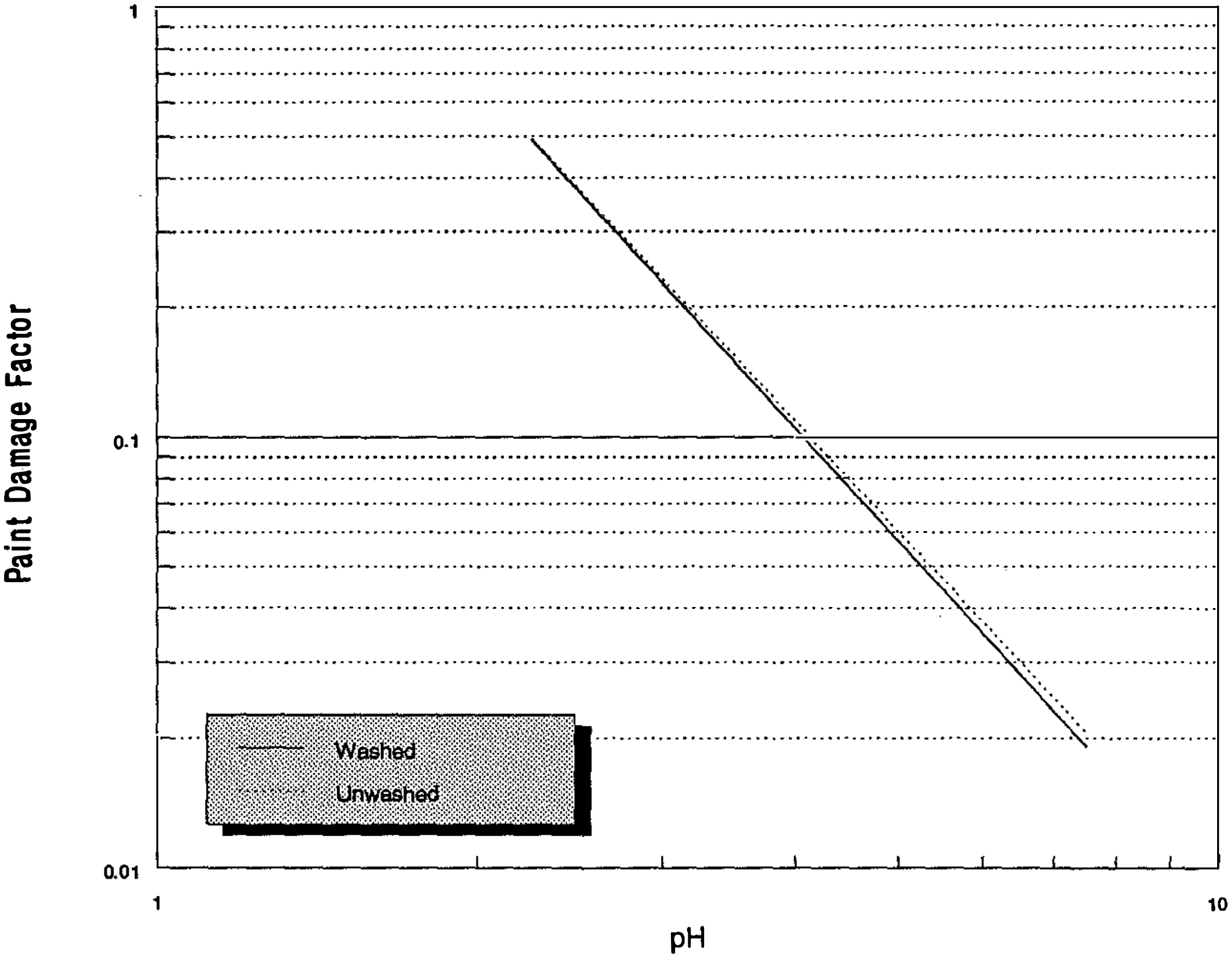


Figure 19. Plot of Paint Damage Factor vs pH for All Soak Tests Performed at 110 °F - Washed (r^2=0.67) and Unwashed (r^2=0.51).

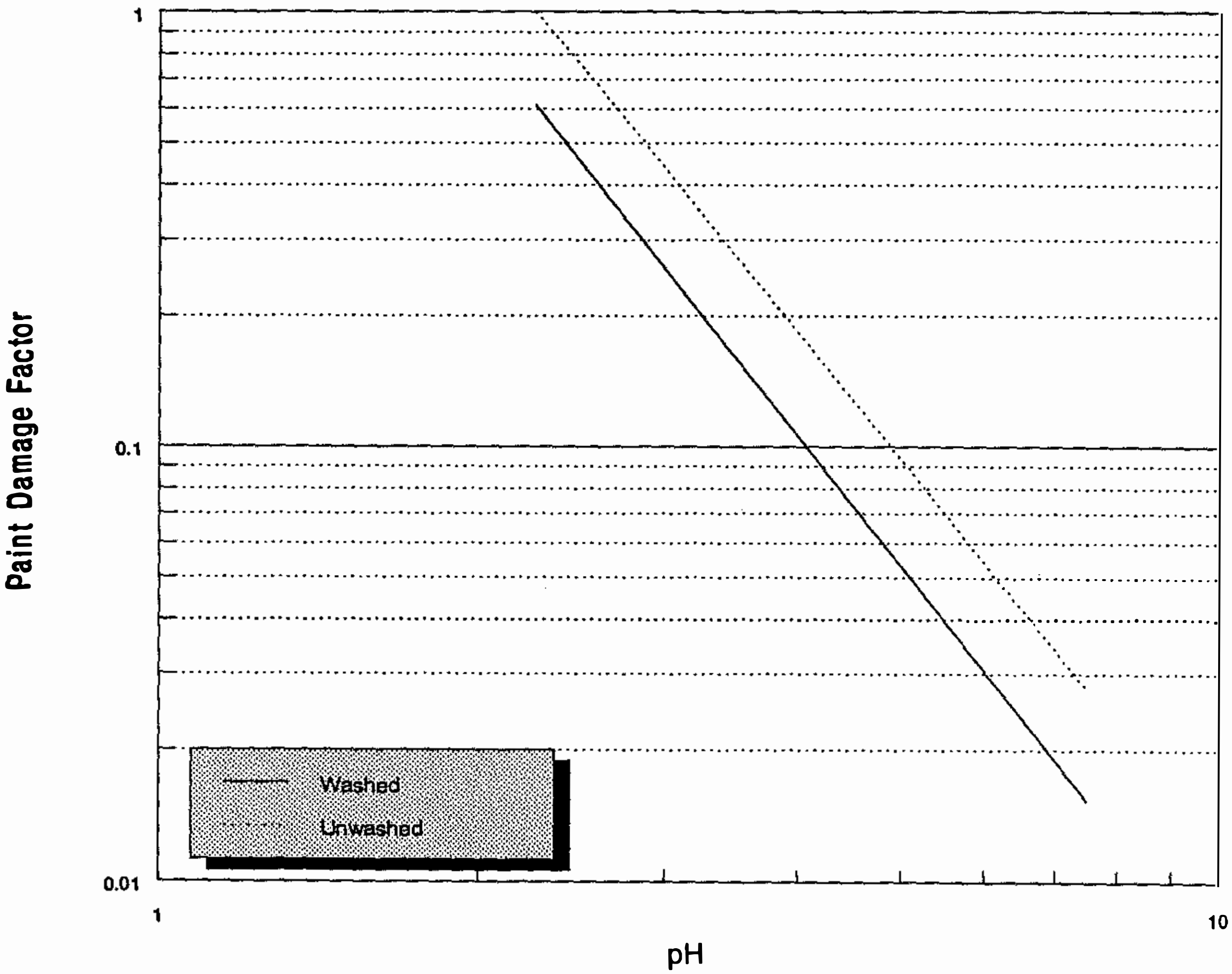


Figure 20. Plot of Paint Damage Factor vs pH for All Soak Tests Performed at 150 °F - Washed (r^2=0.67) and Unwashed (r^2=0.67).

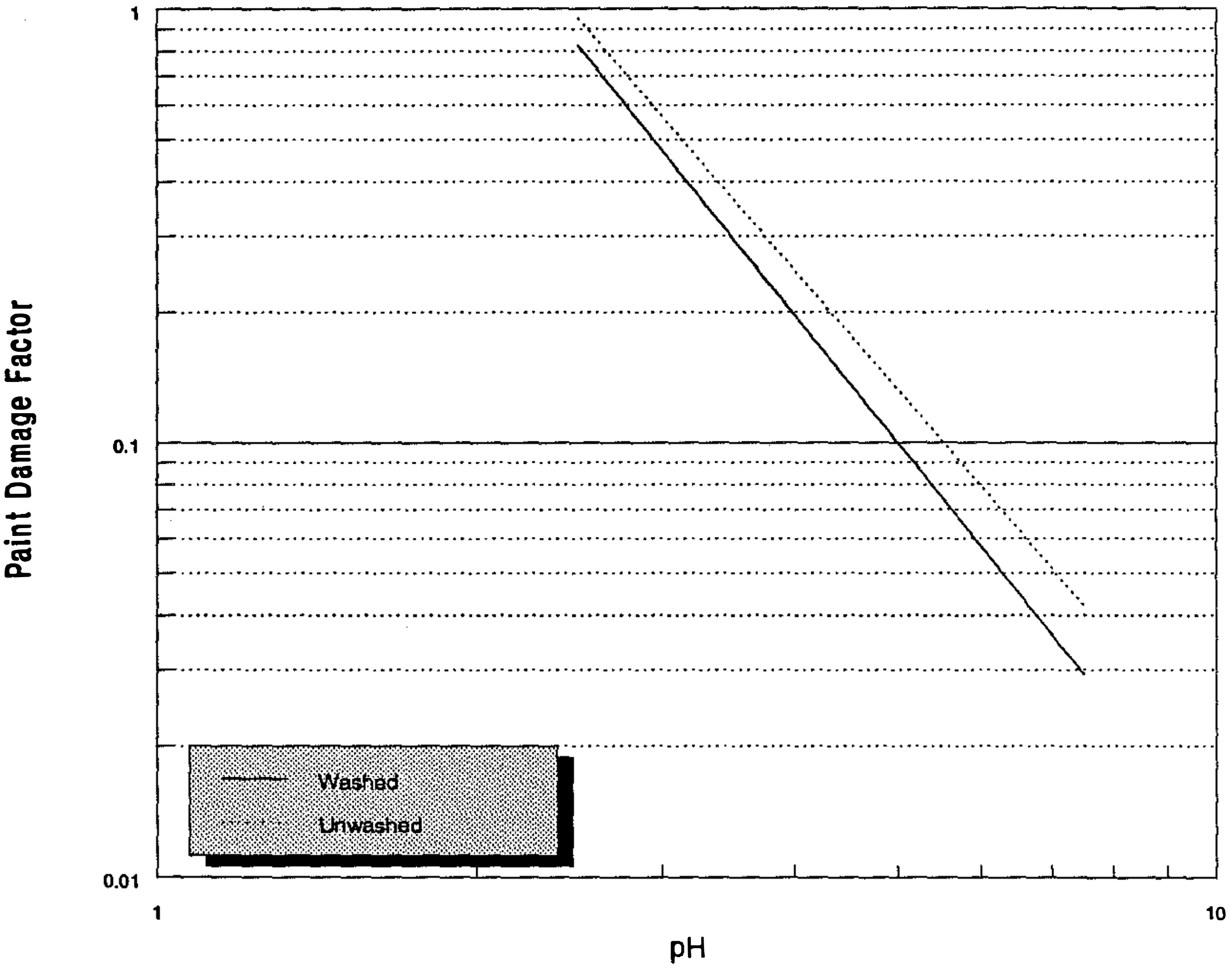


Figure 21. Plot of Paint Damage Factor vs pH for All Soak Tests Performed at 170 °F - Washed (r^2=0.83) and Unwashed (r^2=0.79).

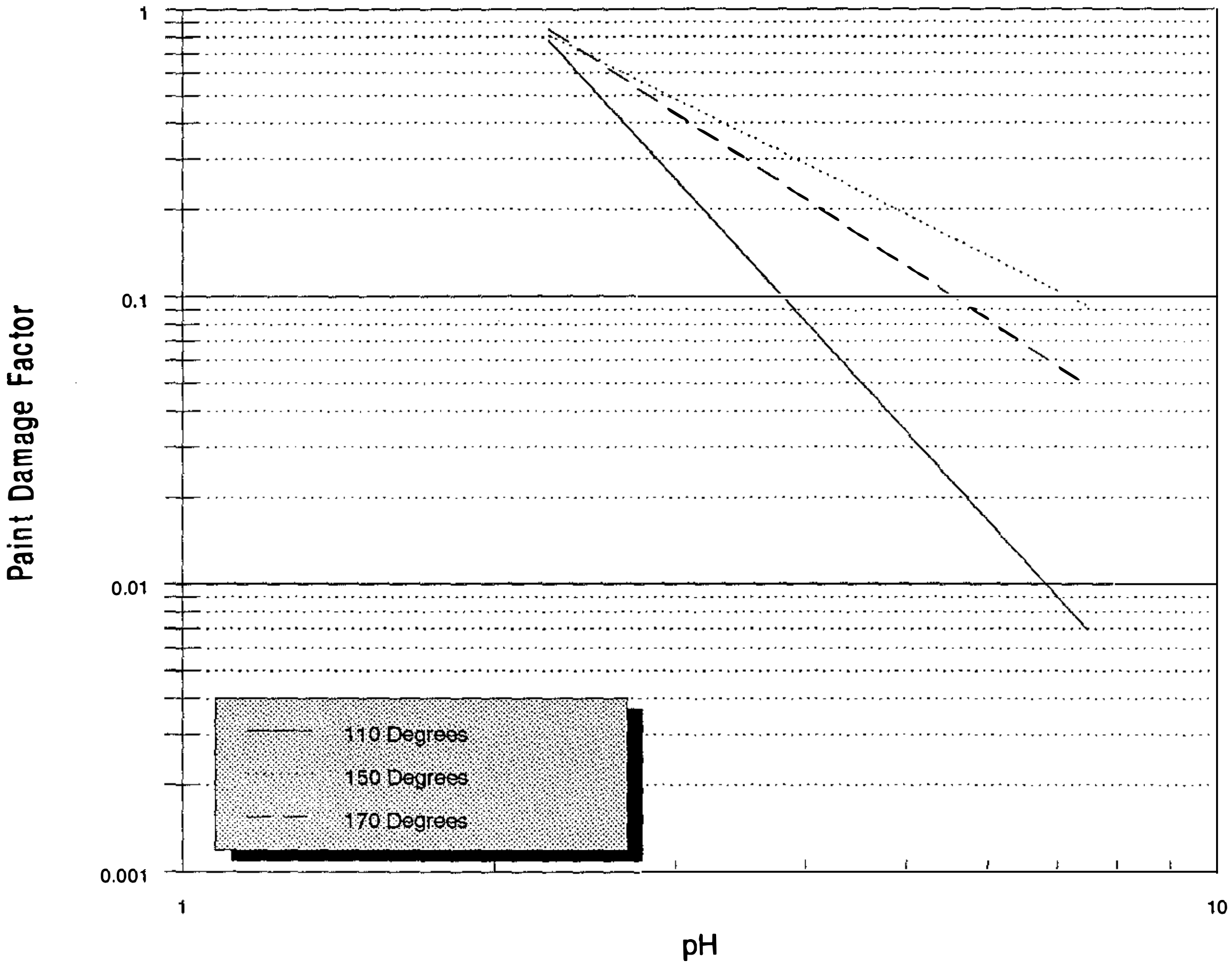


Figure 22. Plot of Paint Damage Factor vs pH for All Soak Tests Performed on White Specimens - 110 °F (r^2=0.99), 150 °F (r^2=0.69), and 170°F (r^2=0.59).

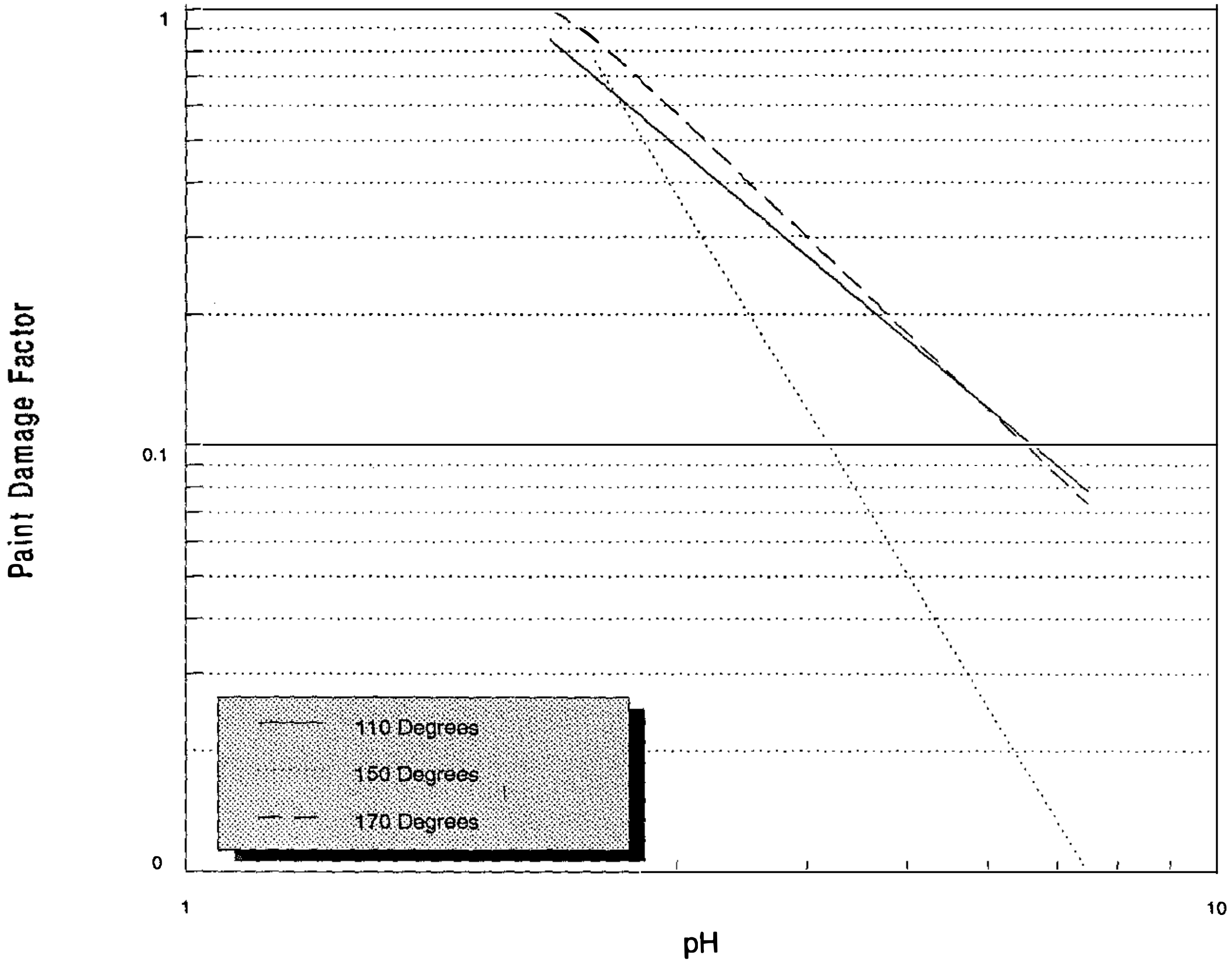


Figure 23. Plot of Paint Damage Factor vs pH for All Soak Tests Performed on Light Blue Specimens - 110 °F (r^2=0.78), 150 °F (r^2=0.75), and 170°F (r^2=0.71).

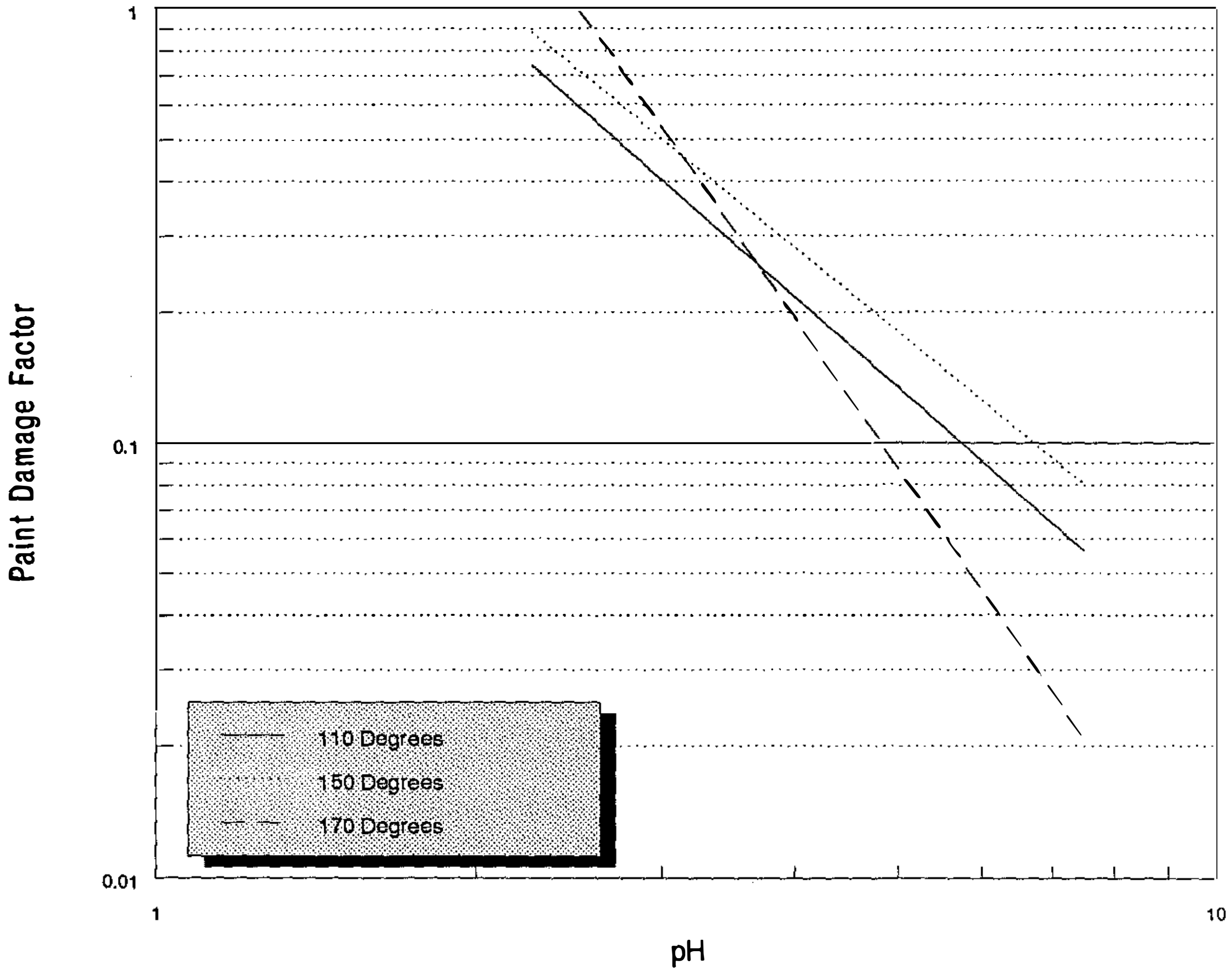


Figure 24. Plot of Paint Damage Factor vs pH for All Soak Tests Performed on Dark Blue Specimens - 110 °F (r^2=0.70), 150 °F (r^2=0.88), and 170°F (r^2=0.73).

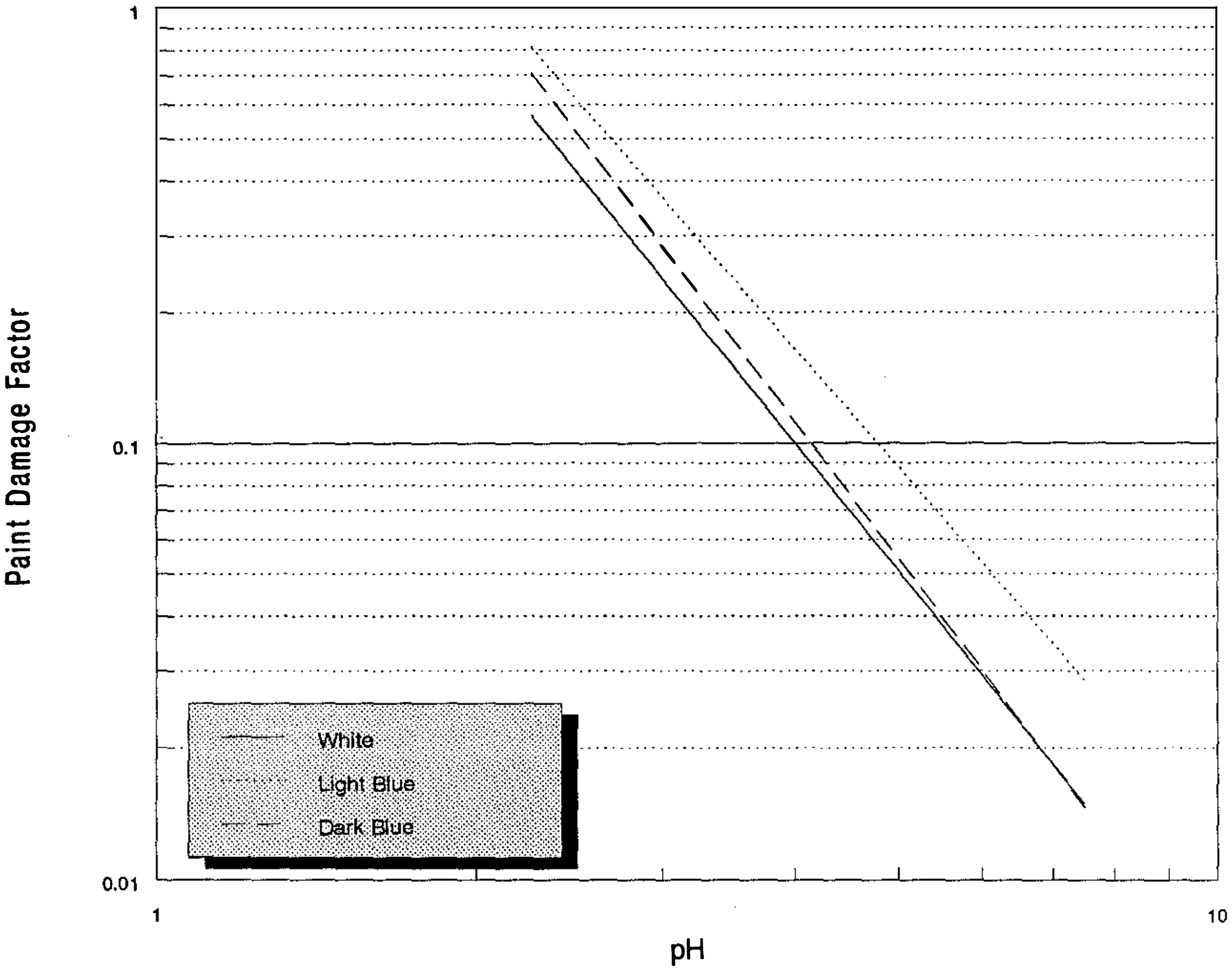


Figure 25. Plot of Paint Damage Factor vs pH for All Soak Tests Using Washed Specimens Showing the Effect of Paint Color - White (r^2=0.59), Light Blue (r^2=0.72), Dark Blue (r^2=0.67).

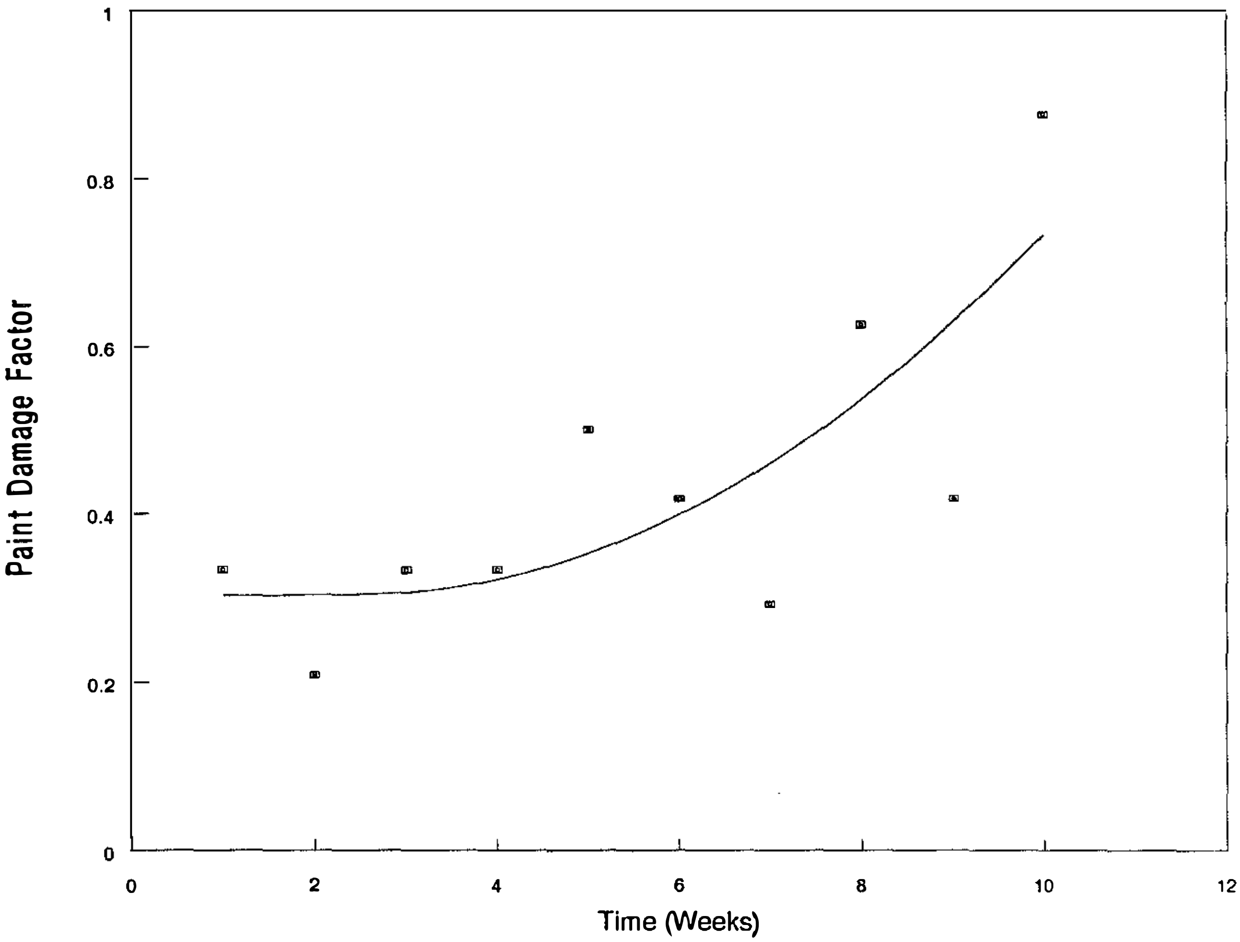


Figure 26. Plot of Paint Damage Factor vs Exposure Time (Weeks) for Field Exposure Tests - Light Blue Specimens (r^2=0.61).

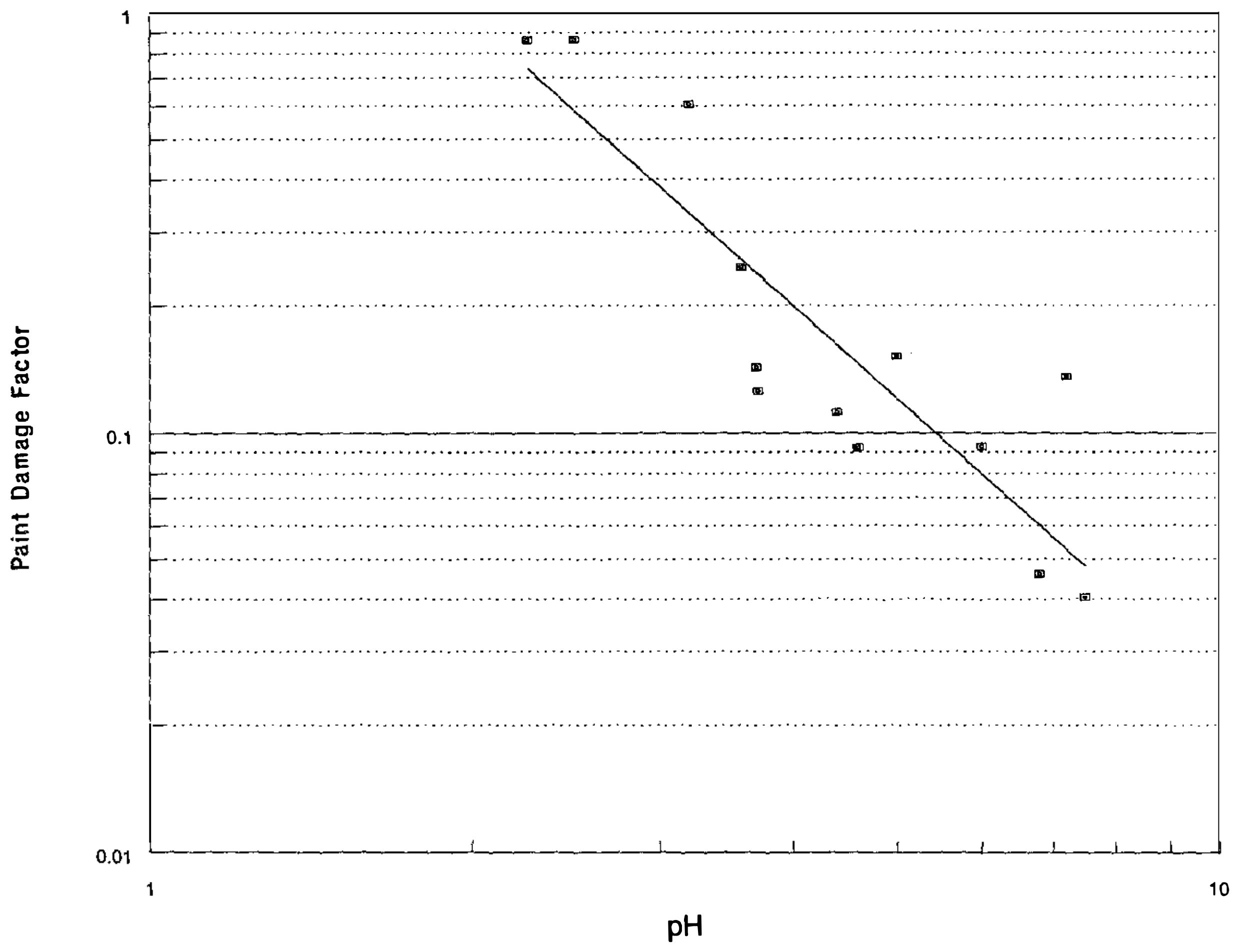


Figure 27. Plot of Paint Damage Factor vs pH - All Tests (r^2=0.78).

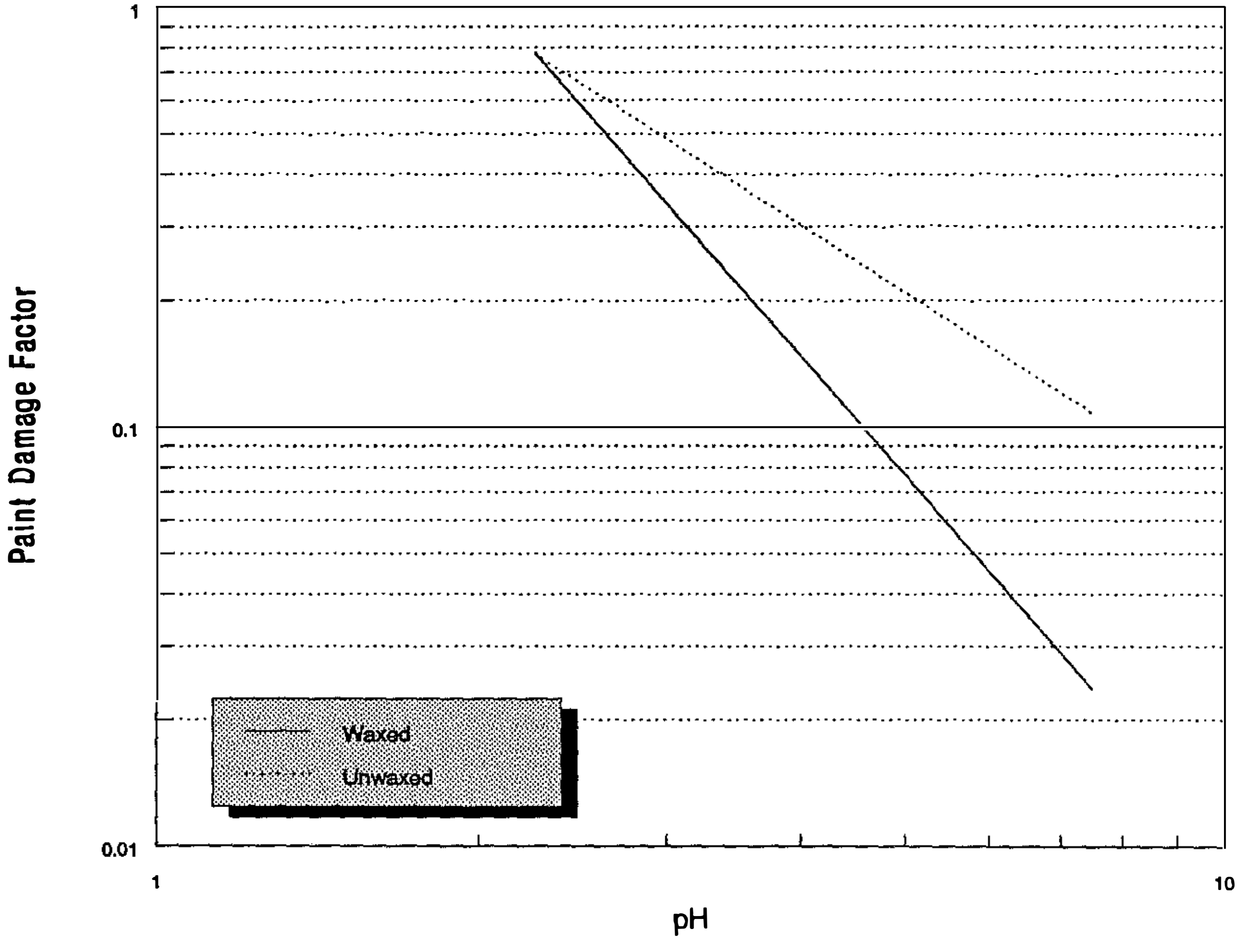


Figure 28. Plot of Paint Damage Factor vs pH for All Tests Comparing Waxed and Unwaxed Specimens - Waxed (r^2=0.84) and Unwaxed (r^2=0.59).

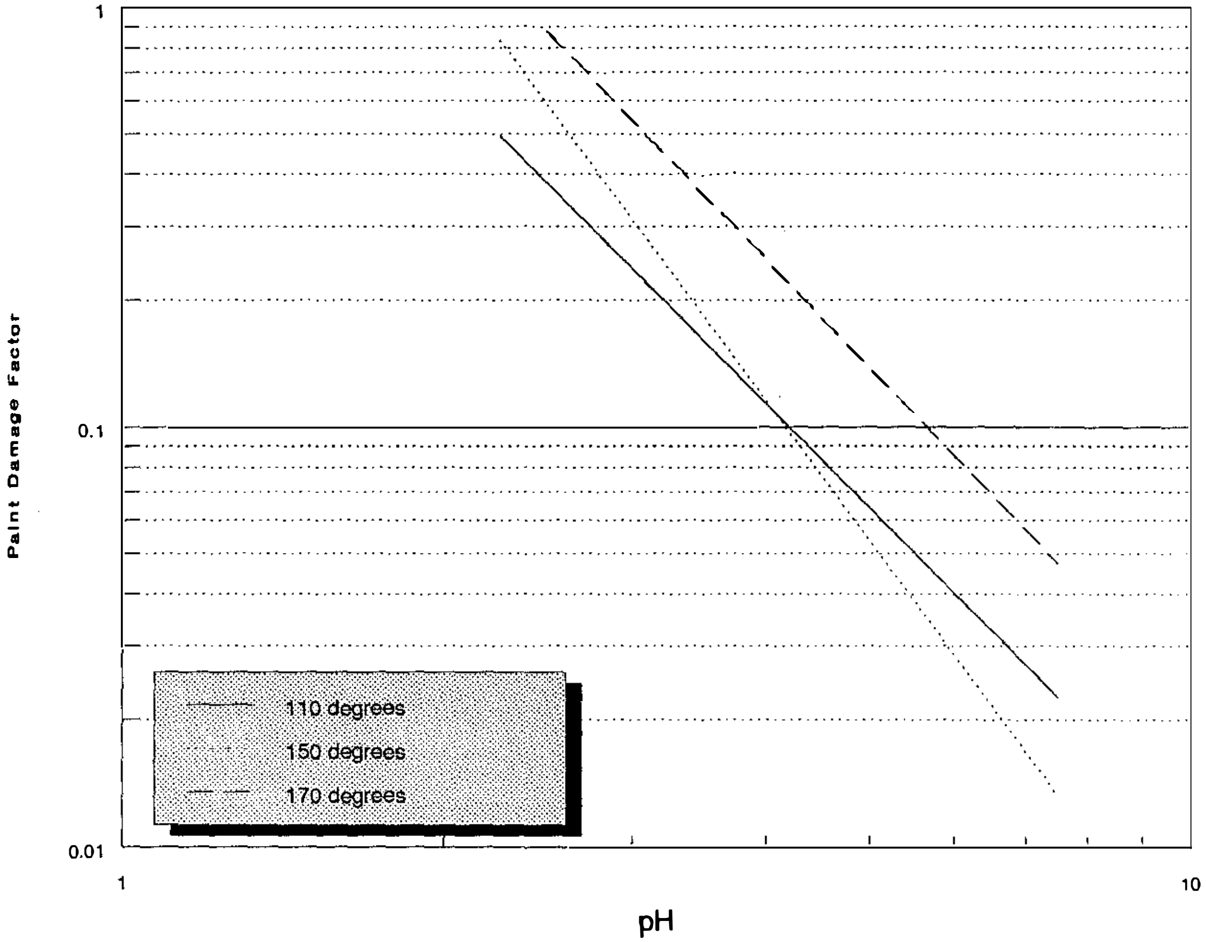


Figure 29. Plot of Paint Damage Factor vs pH for All Tests Performed on Waxed Specimens - 110 °F (r^2=0.61), 150 °F (r^2=0.84), and 170°F (r^2=0.86).

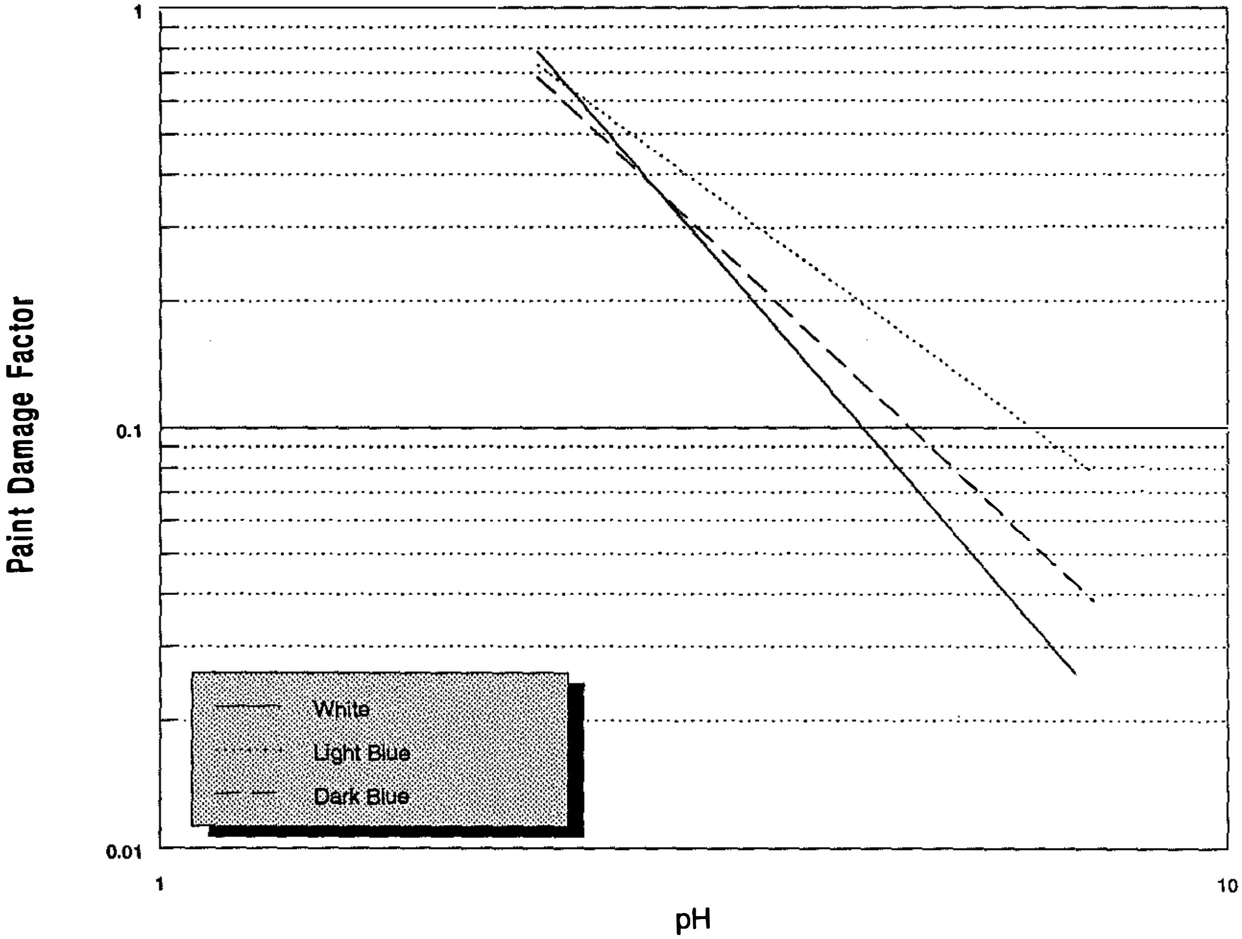


Figure 30. Plot of Paint Damage Factor vs pH for All Tests Showing the Effect of Paint Color - White (r^2=0.79), Light Blue (r^2=0.75), and Dark Blue (r^2=0.63).

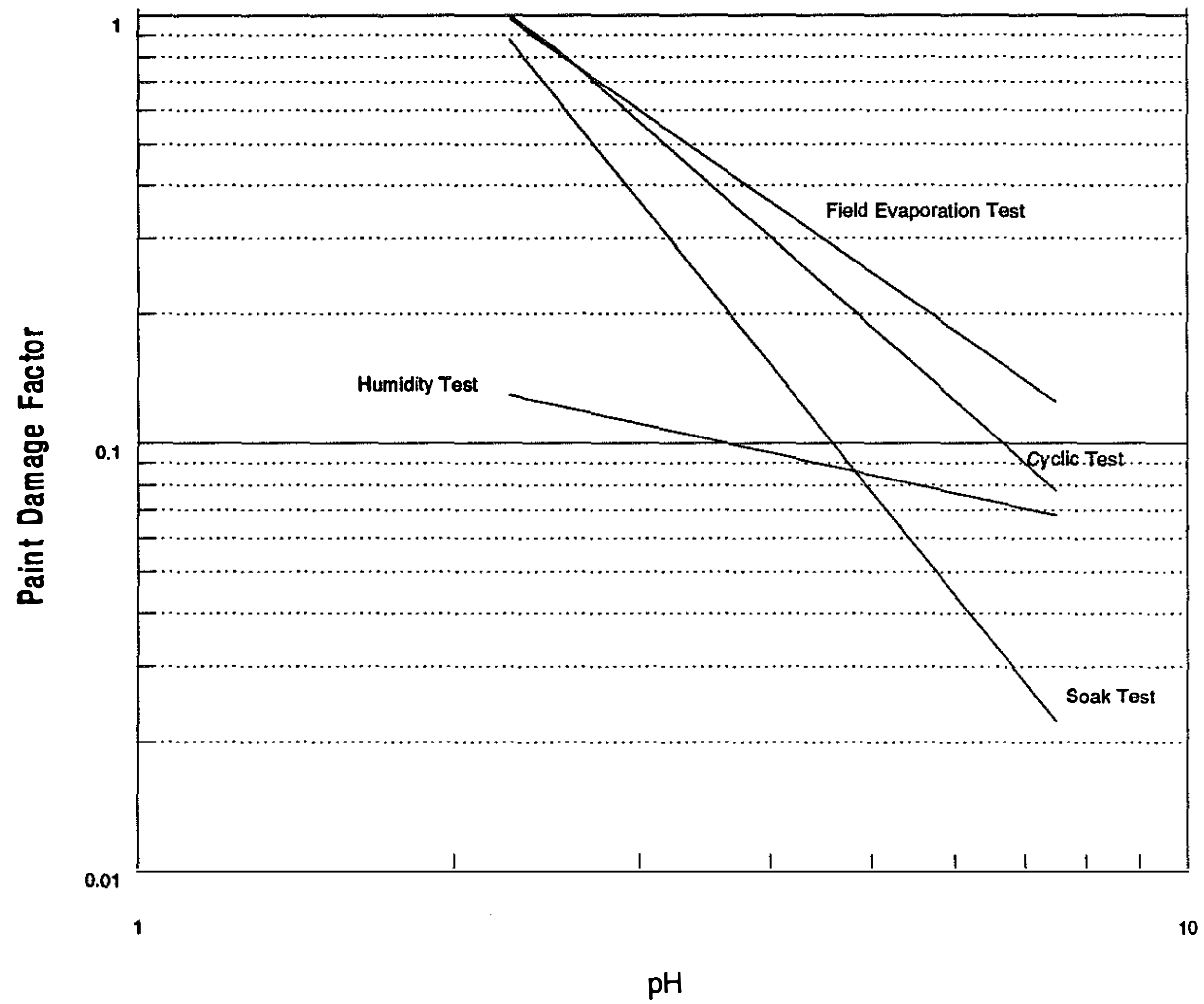


Figure 31. Plot of Paint Damage Factor vs pH for All Tests Showing the Effect of Test Method - Cyclic Evaporation Tests (r^2=0.89), Soak Tests (r^2=0.85), Humidity Exposure Tests (r^2=0.79), and Field Exposure Tests (r^2=0.84).

APPENDIX 3

(Evaluation of Westley's Acid Rain Damage Treatment)

UK UNIVERSITY
OF KENTUCKY
COLLEGE OF ENGINEERING
KENTUCKY TRANSPORTATION CENTER
TRANSPORTATION RESEARCH BUILDING
533 S. LIMESTONE STREET
LEXINGTON, KENTUCKY 40506-0043

MEMORANDUM

July 7, 1990 H.5.133

TO: Jim Funk

FROM: Chris Oberst

SUBJECT: ACID RAIN TESTS - CALIFORNIA SAMPLES

The acid rain tests involved eight 4 x 6 inch painted samples. Four were painted red and four were black. A template was made to indicate the values and locations of four aqueous solutions used in the tests. Those solutions had pH values of 2.2, 3.7, 4.8, and 6.0. The specimens were exposed to different numbers of evaporation cycles. Each cycle consisted of the deposition of a small droplet of a solution followed by its complete evaporation in an oven. Each droplet had a volume of approximately 0.02 ml. The oven temperature was 150°F. One, five, and twelve evaporation cycles were used for each color. Six samples were cleaned after the prescribed number of cycles were completed. Two additional samples were tested at twelve cycles, but were not cleaned after testing.

The final portion of our testing involved applying **Westley's Acid Rain and Spot Remover** to each sample. Below are the test results of each sample prior to and after the product was applied.

Sample	**Observed Results**
A-1 (Red) (1 cycle)	Faint acid rain damage was visible when the sample was held under fluorescent light at the proper angle. Damage was confined to the middle of the sample (pH = 2.2). That damage was largely removed with an application of the Westley's product. Small crescent-shaped spots remained after the application.
B-1 (Black) (1 cycle)	Same as A-1.

(606) 257-4513 • 1-800-432-0719 In State • FAX # (606) 257-1815 • Bitnet KTC@UKCC
An Equal Opportunity University

A-2 (Red) (5 cycles)	Acid rain damage was visible when the sample was held under fluorescent light at the proper angle. Damage was confined to the middle of the sample (pH = 2.2). The crescent-shaped spots were more visible than those on the one-cycle samples. After applying the Westley's product, the spots were less noticeable. They were still observable after a second application.
B-2 (Black) (5 cycles)	The Westley's product seemed to remove more visible damage on this sample than on A-2. Otherwise, the result is the same as A-2.
A-3 (Red) (12 cycles)	Acid rain damage was visible under normal lighting conditions. Damage was confined to the middle of the sample (pH = 2.2). The Westley's product removed very little visible damage.
B-3 (Black) (12 cycles)	Same as A-3.
A-4 (Red) (12 cycles) (unwashed)	Acid rain damage appeared as white particulate matter before the sample was washed. After washing, the damage was observable under normal light conditions. Damage was located in the middle and first and fourth quadrants (ph = 2.2 and 6.0). The visible damage ranged from water spots to crescent-shaped acid rain etching. After applying Westley's product, little change was noted in the visible damage. An additional application produced no observable changes.
B-4 (Black) (12 cycles) (unwashed)	Same as A-4.

Conclusions

The **Westley's Acid Rain and Water Spot Remover** label states that it gently deep cleans harmful acid rain and water spots from a painted car finish. It further states that acid rain droplets often leave behind white bleach marks which can permanently damage a car's finish if not removed promptly.

In our controlled acid rain test, the Westley's product removed most of the visual acid rain damage on a lightly damaged surface. It was not as effective on severely damaged surfaces. The Wesley's product might be most effective against recently spotted car surfaces. In these tests, it did not remove paint etching which is a common characteristic of severe acid rain damage.

APPENDIX 4

(Surface Temperatures of Cars at Toyota Marshalling Yard)

Vehicle Temperatures Measurements at the Toyota Marshalling Yard

Surface temperature (°F) measurements taken on June 26, 1990 between 1-2 P.M. on vehicles in the Toyota (Georgetown, KY) marshalling yard. The air temperature was in the low 80's with a slight breeze. The sky was clear with no clouds. The pavement temperature was 126 °F.

Color	Trunk	Midpoint of Roof	Hood
Mahogany	147/142	159/154	154/142
Maroon	145/140	153/150	141/138
Dark Blue	142/138	150/148	141/139
Red	135/133	142/141	130/129
Charcoal Grey	134/132	142/141	139/132
Gold	125/120	129/125	123/119
Light Blue	120/115	125/121	113/113
Silver	117/112	123/121	114/113
White	103/101	111/105	103/97

APPENDIX 5

(Microprobe Specifications)

Droplets
Microliter Samples

MICROELECTRODES, INC.
Londonderry, N.H. 03053

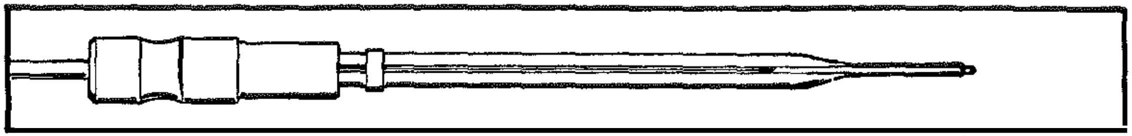
Specialists in the
development and manufacture
of microelectrodes
since 1970!

Catalog No. 098

MICRO-COMBINATION PROBES

Measure pH in less than 1/10 drop. Fast response.

MI-410 MICRO-COMBINATION pH PROBE

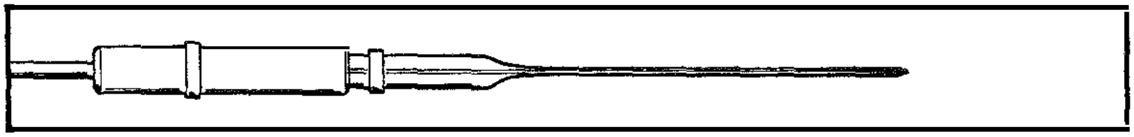


Specifications:

Total length	15 cm
Lead length	1m
Body (Outer Diameter)	6 mm
Tip (Outer Diameter)	pH: 1.2 mm / Ref: 2.5 mm
Sensitivity	pH 0 to 14
Temperature range	-5°C to 100°C
Response time	5 to 15 seconds
Depth of immersion	1.5 to 2 mm
Reference electrode type:	
Solution and electrode	3M KCl and Ag-AgCl

Price (see price list) includes:
1 Combination pH Electrode
1 Bottle of Reference Solution
1 Bushing to fit standard holders

MI-415 MICRO-COMBINATION pH PROBE



Specifications:

Total length	14 cm
Lead length	1 m
Body (Outer Diameter)	6 mm
Tip (Outer Diameter)	pH: 0.75mm/Ref: 1.3mm
Sensitivity	pH 0 to 14
Temperature range	-5°C to 100°C
Response time	5 to 15 seconds
Depth of immersion	0.5 to 1.0 mm
Reference electrode type:	
Solution and electrode	3M KCl and Ag-AgCl

Price (see price list) includes:
1 Combination pH Electrode
1 Bottle of Reference Solution
1 Bushing to fit standard holders

★ Available in 2, 4, or 6 cm Tips ★

pH

MI-410 / MI-415 OPERATING INSTRUCTIONS

MICROELECTRODES, INC.
Londonderry, New Hampshire 03053
U.S.A.
(603) 668-0692

MI-410 and MI-415
Micro-Combination pH Electrode Operating Instructions

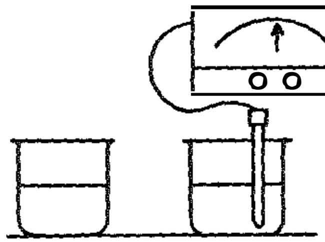
Use of the Electrode

The electrode is ready to use. Carefully unwind the tape and remove the probe from the protective glass tube. The white sleeve which covers the fill-hole should be moved down the glass barrel to ventilate the reference chamber and replaced after use.

Calibration

The probe can be inserted into your electrode holder with the use of the reducing bushing provided or held by hand when measuring pH. The probe is standardised in two (2) pH buffers. Check instructions enclosed with your pH meter for correct procedure.

Optimum response time will be obtained after the probe has been exercised in two (2) buffer solutions. Place a pH 4.01 buffer in a 50 ml beaker and a pH 6.86 buffer in a second 50 ml beaker (other beakers can also be used). Hold the probe and touch the pH 4.01 buffer surface allowing 5 seconds for equilibration, and then touch the pH 6.86 buffer surface in the same manner. Do this several times. It is not necessary to rinse the probe with distilled water because the carryover is negligible.



Handling, Cleaning, and Storing of Electrode

Handling: When necessary the outer reference chamber of the electrode can be refilled using the 3 M KCl dispensing bottle provided with the probe. This may be a slow process but introducing syringe needles or plastic tubes into the fill-hole generally results in breaking the inner glass capillary rendering the probe inoperative.

> *Care must be taken that the delicate inner glass capillary is not cracked when refilling. Do not apply pressure against the inner glass capillary tube.*

Cleaning: When using the electrode in solutions containing protein, the electrode should be soaked in an enzyme cleaning solution such as our A-50 Cleaning Solution or a chromic/sulfuric acid glass cleaning solution after each use for a couple of minutes to remove the protein from the glass and the reference junction. This will prolong the useful life of the probe.

Storing: Always clean the electrode before storing.

Long-term (over 2 weeks): return electrode to its original container and prepare it in the same condition in which you received it. Usually this means simply moistening the sponge located in the bottom of the protective glass tube with distilled water.

Short-term: the electrode can be left in an acid pH buffer solution, e.g. pH 4.01.

Troubleshooting

A. Little or No Response:

Inspect the electrode for visible cracks (usually occuring around the tip of the electrode). If any exist, the electrode cannot be rejuvenated and must be replaced. The slightest crack in or around the membrane will cause the electrode to read about the same in all solutions.

B. Response Pegs Off Scale:

1. Visually inspect the electrode for broken or dissolving internal elements or for inadequate volume of filling solution. Filling solution level should be above the internal elements.

2. Blocked or clogged liquid junction - soak the tip of the electrode in warm (60° C) distilled water for 5 to 10 minutes. If still clogged, then soak overnight in distilled water.

C. Sluggish Response:

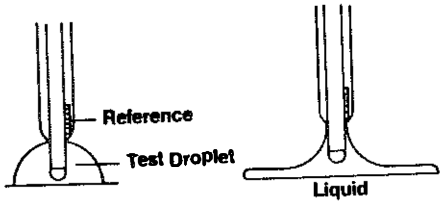
If the probe becomes sluggish in responding to changes in pH, the response time can be improved by soaking in 0.1 N HCl for 5 minutes followed by soaking in 0.1 N NaOH for 5 minutes. After doing this several times, the probe can then be calibrated in the usual manner.

☎ *For additional assistance, call our customer service department at (603)668-0692.*

MICROELECTRODES,INC.
LONDONDERRY, NEW HAMPSHIRE 03053
U.S.A.
(603) 668-0692

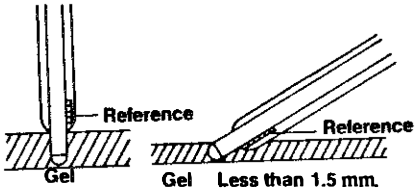
A: SMALL VOLUMES

The reference junction must make contact with the solution.
When the PROBE touches the surface of liquid, the surface tension will be such that contact is made with the reference junction.



B: GELS

For gel thicknesses less than 1.5 mm, the probe can be held at an angle such that the reference junction touches the gel.
The reference junction is on the same side as the fill hole.
The gel thickness should be about 1.5 mm.



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pH

MI-410 / MI-415 OPERATING INSTRUCTIONS

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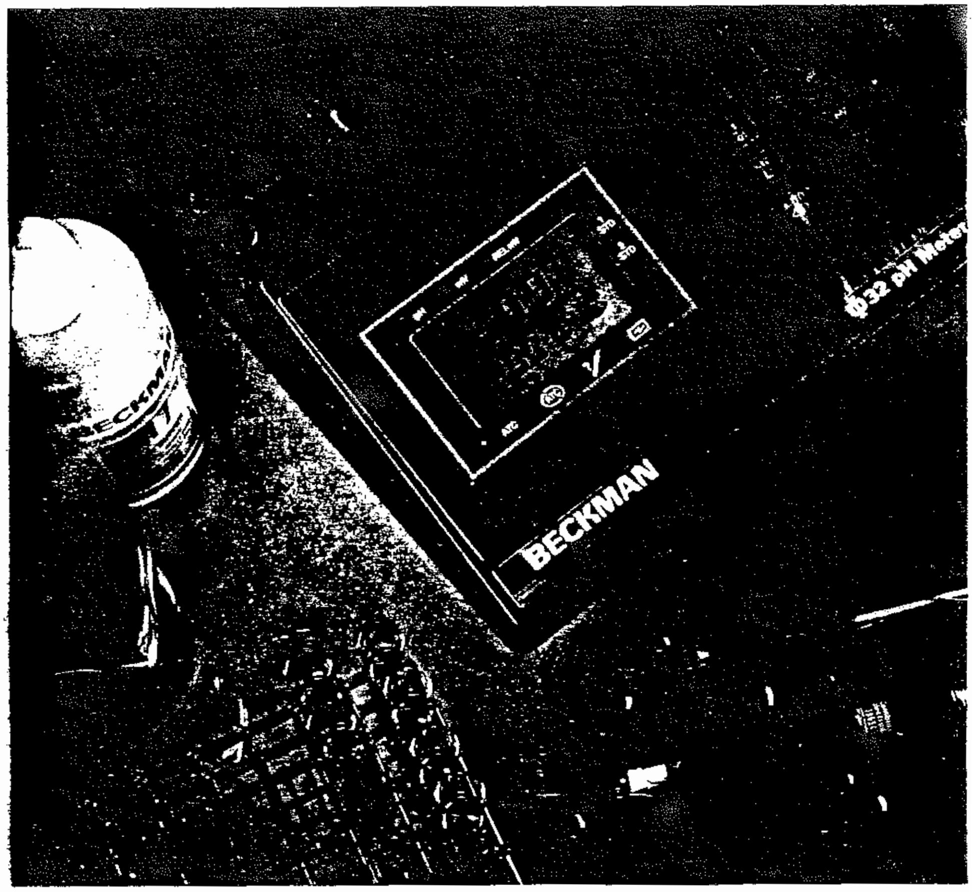
(603) 668-0692

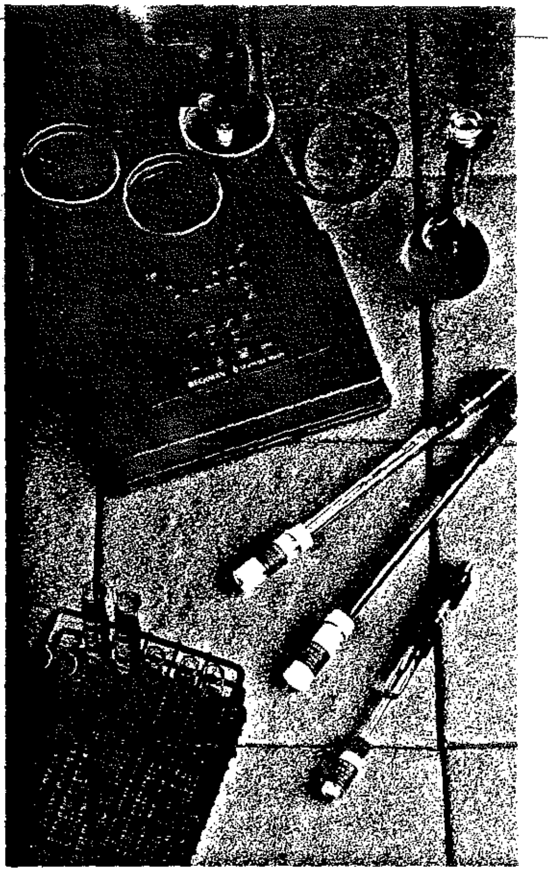
Bulletin No. 7831

pHI™ Series
pH Meters, Electrodes and Accessories



BECKMAN

The economical pHI 10 for pH only and the pHI 11 to measure pH, millivolts and relative millivolts.



The pHI 12 is both a pH and an ion-selective meter, with pH, mV and concentration measurements.

pHI 10 and 11: Small Size. Big Performance.

The pHI 10 and 11 fit almost anywhere and offer the same precision and ease of use as benchtop models. Factory Mutual approved for use in Class I, Groups A, B, C, and D, flammable environments.

pH Resolution:	Selectable 0.01/0.1
mV Resolution:	0.1 (pHI 11 only)
Temp Resolution:	0.1°C

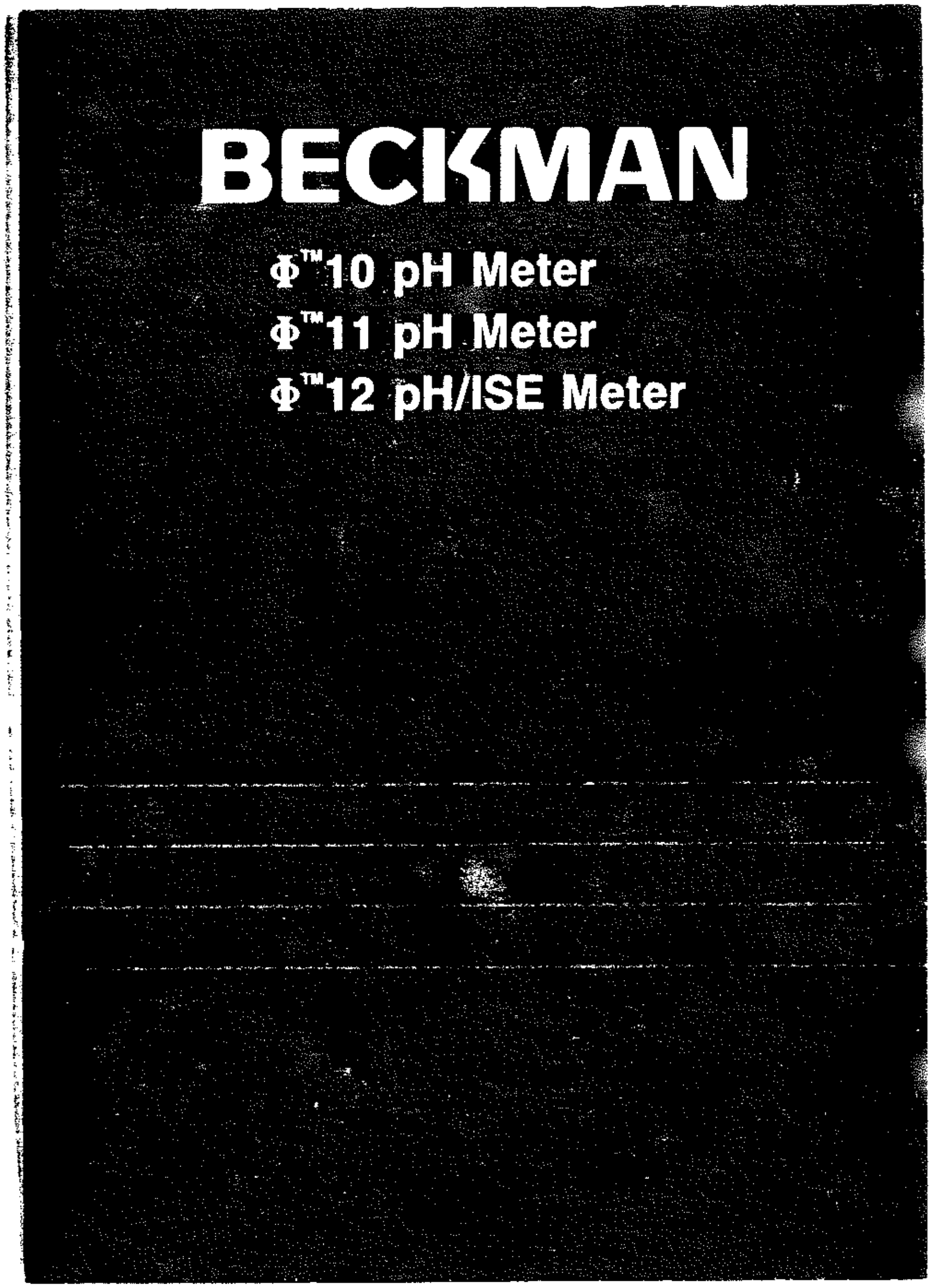
Ideal for classrooms, field use, research, and pharmaceuticals.

pHI 12: pH Portability With Ion-Selective Capability.

Factory Mutual approved for use in Class I, Groups A, B, C, and D, flammable environments.

pH Resolution:	Selectable 0.01/0.1
mV Resolution:	0.1
Temp Resolution:	0.1°C
Concentration Range:	0.01-8000, Selectable Units

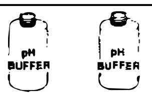
Also ideal for classrooms, field use, research, and pharmaceuticals.

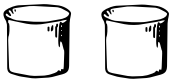
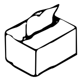
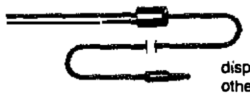


BECKMAN

Φ™10 pH Meter
Φ™11 pH Meter
Φ™12 pH/ISE Meter

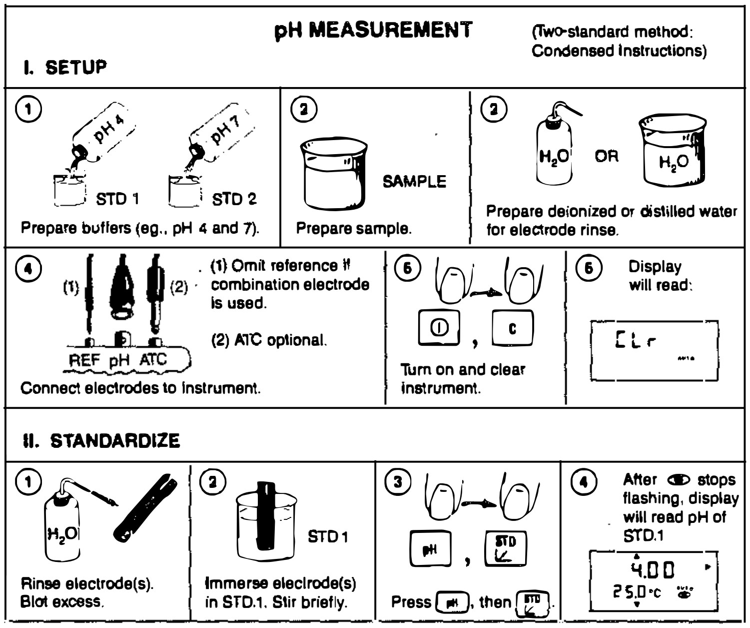
FOR ACCURATE pH MEASUREMENTS WITH THE Φ10, Φ11, OR Φ12, THE FOLLOWING ITEMS ARE RECOMMENDED:

1.		**pH indicating** electrode, Futura Plus. **Cable with BNC** connector, Futura.
AND		**Reference** electrode, Futura Plus. **Cable with 2 mm pin** connector, Futura.
OR		
1. (ALT.)		**Combination** electrode, Futura Plus. **Cable with BNC** connector, Futura.
2.		**Any two** of the following standard pH buffers: **1.68 4.00 7.00 10.01 12.45**

3.		Two clean beakers or equivalent containers, approximately 100–250 mL, for containing the two standard buffers.
4.	 OR 	Squirt bottle or beaker containing deionized or distilled water for rinsing electrodes.
5.		Clean towels, "Kimwipes™", etc., for blotting electrodes.
6.		598115 Automatic Temperature Compensator (ATC) probe. Required if measurement and display of temperature or compensation for temperatures other than 25°C is desired.
7.	 SAMPLE	The sample to be measured

For part numbers, see "Electrodes, Buffers, and Accessories."
For pH measurement procedure, see next page.

MEASURING pH (Φ10, Φ11, Φ12)



pH MEASUREMENT

(Two-standard method: Condensed Instructions)

I. SETUP

① Prepare buffers (eg., pH 4 and 7).

② Prepare sample.

③ Prepare deionized or distilled water for electrode rinse.

④ Connect electrodes to instrument.

(1) Omit reference if combination electrode is used.

(2) ATC optional.

⑤ Turn on and clear instrument.

⑥ Display will read:

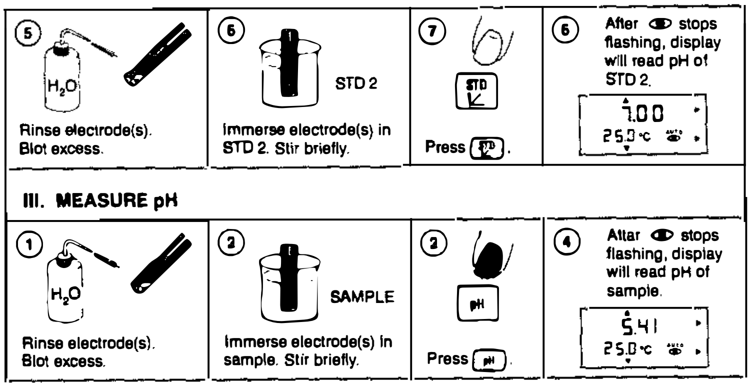
II. STANDARDIZE

① Rinse electrode(s). Blot excess.

② Immerse electrode(s) in STD.1. Stir briefly.

③ Press pH, then STD.

④ After ◉ stops flashing, display will read pH of STD.1



⑤ Rinse electrode(s). Blot excess.

⑥ Immerse electrode(s) in STD 2. Stir briefly.

⑦ Press STD.

⑧ After ◉ stops flashing, display will read pH of STD 2.

III. MEASURE pH

① Rinse electrode(s). Blot excess.

② Immerse electrode(s) in sample. Stir briefly.

③ Press pH.

④ After ◉ stops flashing, display will read pH of sample.

APPENDIX 6

(Chemical Characterization for a Monitoring Network in the Lower Ohio Valley)

Chemical Characterization of Precipitation from a Monitoring Network in the Lower Ohio River Valley

Rick D. Saylor (1) Kevin M. Butt (1)* Leonard K. Peters (2)

(1) Center for Applied Energy Research
University of Kentucky
Lexington, KY 40511-8433

(2) Department of Chemical Engineering
University of Kentucky
Lexington, KY 40506-0046

[submitted to Atmospheric Environment February 1991]

Abstract

The Kentucky Acid Deposition Program (KADP) precipitation chemistry network was initiated in 1983 with the goal of providing a statewide monitoring system to document the occurrence of acid deposition in Kentucky. A variety of analyses have been performed on the KADP data for the period 1983-1989 to characterize precipitation chemistry in the lower Ohio River Valley. H_2SO_4 and HNO_3 are identified as the primary contributors to precipitation acidity in this region, with HCl playing a secondary role. Neutralization of precipitation acidity occurs both as a result of the dissolution of alkaline soil dust compounds containing Ca^{++}, Mg^{++}, and K^+ as well as the absorption of NH_3 vapor. H^+, $SO_4^=$, and NO_3^- precipitation concentrations exhibit a seasonal pattern in which higher concentrations are observed during summer months and lower concentrations during winter months. The seasonal behavior of NH_4^+ concentrations, however, differs from this pattern in that the highest concentrations occur during spring months while the lowest values occur during autumn. Annual depositions of $SO_4^=$, NO_3^-, Cl^-, NH_4^+, Ca^{++}, and H^+ show no apparent qualitative temporal trend over the 1985-1989 period in this region.

Keywords: precipitation chemistry, acid rain, chemical deposition, statistical analysis, monitoring network

*Current address: ARMCO Steel Co., L.P., PO Box 191, Ashland, KY 41101

1. Introduction

The Kentucky Acid Deposition Program (KADP) precipitation chemistry network was initiated in 1983 with the goal of providing a statewide monitoring system to document and characterize the occurrence of acid deposition in Kentucky. This monitoring network was developed and is operated by the research staff of the Environmental and Materials Research Division of the University of Kentucky Center for Applied Energy Research (UKCAER). The network database is intended for use in advancing the understanding of acid deposition along many fronts including: (1) elucidating the primary chemical and physical atmospheric mechanisms responsible for the transport and transformation of acid precursor pollutants; (2) determining the statewide variation of acid deposition; (3) investigating the role of local emission sources on intra- and inter-state acid deposition; (4) assessing the effects of acid deposition on aquatic and terrestrial environments within the state; and (5) providing empirical data for the development and validation of numerical atmospheric transport/transformation/deposition models.

Monitoring stations in the KADP network are shown in Figure 1 and further described in Table 1. This area in the lower Ohio River valley is of particular interest due to its high density of major pollutant emission sources. In fact, the states of Ohio, Indiana, Illinois, and Kentucky account for over one-fourth of the total point source SO_2 and approximately one-fifth of the total point source NO_x emitted from the contiguous U. S. annually (Wagner et al., 1986). Between 1983 and 1989, up to ten monitoring sites have been in active operation at once; as of January 1, 1990, all sites listed in Table 1 were active except for Hope Creek, which was taken out of service in 1988.

The objectives of the current work are to: (1) characterize the chemical composition of precipitation in the lower Ohio River Valley; (2) statistically analyze the six-year precipitation chemistry database to determine relationships between the various ionic species; and (3) begin to look for long-term trends in acidic deposition occurring over the region. The analyses presented in this paper were performed using data from the KADP network from its initiation in late 1983 through December 1989.

2. Experimental Methods

2.1 Sample collection and analysis

The majority of the KADP monitoring stations are located within Kentucky State Parks and are operated by park personnel on a voluntary basis. One exception is the Perryville Battlefield State Park site which is part of the National Atmospheric Deposition Program/National Trends Network (NADP/NTN) and is operated by UKCAER research staff. Each monitoring station is located within a chain-link fence (6-feet in height) enclosing an area of approximately 10 feet by 20 feet. The sampling equipment within each enclosure includes an Aerochem Metrics Model 301 wet and dry deposition sampler and a Belfort 5-780 Series rain gauge with an event recorder pen. Wet deposition samples are collected in standard 13 L polyethylene buckets on a weekly basis every Tuesday morning at 9:00 am. Sample collection protocols are designed to follow NADP/NTN procedures (Bigelow and Dossett, 1988) as closely as possible. After collection, the buckets are tightly sealed with a clean polyethylene lid, packaged for shipment, and sent to UKCAER for chemical analysis. Samples from the Perryville Battlefield site are shipped to and analyzed at the Central Analytical Laboratory in Champagne, Illinois as part of the NADP/NTN.

The chemical species routinely measured in each precipitation sample are listed in Table 2 along with associated analytical procedures, instruments, and minimum detection limits. The conductivity and pH of each sample are measured within 24 h after arrival at the UKCAER laboratory. Incoming samples are first weighed to determine precipitation volume; 100 ml aliquots are then drawn, filtered, and stored in clean polyethylene bottles. These aliquots are stored in the dark at 4° C until analysis, which typically occurs within one month following initial collection. All buckets, bottles, and other laboratory accessories in contact with precipitation samples are carefully washed with double-distilled/de-ionized water with a specific conductance of < 2 microS cm^{-1} and are air-dried, enclosed, and stored in clean polyethylene bags until use.

All field equipment is routinely inspected by on-site operators for proper operation. In the event of equipment failure, technicians are sent from UKCAER to the site as soon as possible to minimize downtime. Annually, a detailed site audit is performed for each monitoring station to ensure the proper calibration and operation of each piece of sampling equipment as well as to remind the on-site operator of proper collection procedures.

2.2 Data editing procedures

There are many possible sources of error in the measurement of precipitation chemistry and the analysis of data from monitoring networks. Some of these sources include analytical measurement errors, contamination resulting from poor collection techniques, and even contamination from uncontrollable outside influences (e.g., bird droppings, windblown tree leaves, dust, etc.). In performing the present analysis we attempted to identify and delete samples which were obviously contaminated or questionable. Several criteria were used to determine the suitability of a particular sample for inclusion in further statistical analyses.

First, a sample could not be obviously contaminated; i.e., if the sample was discolored or contained insects or other foreign material. Secondly, the sample had to be wet-only deposition. A wet deposition sample was defined as one that has been exposed to dry deposition for less than 6 h per weekly sampling period. The third criterion was that the sample had to be a true weekly sample, defined as having a sample age of greater than 6 days but less than 8 days. A fourth criterion required that the precipitation collector efficiency for a particular sample be greater than 0.5. The collector efficiency is defined as the ratio between calculated precipitation amount (as determined from the sample weight) and the measured rain gauge amount.

A final screening procedure attempted to detect analytical measurement errors or non-obvious contaminated samples using an outlier analysis. This outlier analysis consisted of the following six steps: (1) for each ionic species the geometric mean and standard deviation were calculated; (2) all data points that were more than two standard deviations away from the mean were designated as possible outliers; (3) each of these questionable data points was then investigated in detail to determine whether justification existed for its removal from the data set; (4) if the investigation of a certain questionable sample revealed possible contamination, it was removed from the database used for statistical analysis; (5) if the investigation revealed no source of contamination, then the questionable sample was reanalyzed; and finally (6) if the sample reanalysis differed substantially from the original analysis, the sample was removed from the statistical database.

3. Results of data analyses

3.1 General relationships

From the initiation of the KADP network in late 1983 through December 1989 a total of 1845 samples have been obtained from ten monitoring stations. After data editing, a total of 1670 samples have been included in the statistical analysis database. For each species, minimum and maximum values, arithmetic means, geometric means, and volume-weighted means have been calculated for data from each site and for the entire data set for various averaging times. Details of these statistics are available in Saylor (1989), while averages for the entire 1983-1989 period are presented in Table 3. To investigate seasonal variability, monthly volume-weighted concentrations were determined. In order to study relationships between specific ions, correlation coefficients for all possible ion pairs were calculated for each site and for all data. Additionally, to identify which ions most affect precipitation acidity, multiple regression analyses were performed using hydrogen ion concentration as the dependent variable and the other ion concentrations as independent variables. The average relative magnitude of ionic species concentrations from the network follows the relation $SO_4^= > H^+ > NO_3^- > NH_4^+ > Ca^{++} > Cl^- > Na^+ > Mg^{++} > K^+$. This relative abundance relationship holds for arithmetic and geometric mean concentrations, as well as for volume-weighted mean concentrations.

A typical frequency distribution of ionic species concentrations is illustrated in Figure 2 for H^+ ion. The distribution is not normally distributed but is skewed toward lower concentrations. The H^+ distribution shown in Figure 2 is very typical for most ionic species concentrations in precipitation samples from the KADP network and also from other networks (MAP3S/RAINE, 1982; Likens et al., 1984). Since precipitation chemistry concentration distributions are closer to log-normality than regular normality, the arithmetic mean concentration does not also represent the median concentration. In fact, the geometric (log-normal) mean comes closer to describing the median concentration value.

Figure 3 presents a typical plot of $SO_4^=$ concentrations versus amount of precipitation. Plots for other species are similar in nature. It is observed that the highest ion concentrations generally occur in samples with the smallest amount of precipitation, while low concentrations occur with either low or high amounts of precipitation. As has been postulated by other investigators (Tabatabai and Laflen, 1976; Lindberg, 1982; Likens et al., 1984; and Khwaja and Husain, 1990) there are several possible explanations for this behavior. Below-cloud evaporation at the leading edge of a frontal storm has been offerred as one of these, while simple dilution of species concentrations by large amounts of precipitation is another. Our observations and model results (Saylor, 1989) suggest that the largest ionic concentrations are due to the below-cloud removal of aerosols during brief showers which occur after an extended period of dryness and air stagnation.

A significant motivating factor for precipitation chemistry research is the effect of trace substances in precipitation on aquatic and terrestrial ecosystems. Since these effects are likely to be associated with the total amount of substance deposited, it is more informative to characterize ionic concentrations as precipitation-weighted values (also termed volume-weighted concentrations). In this way the effects of Figure 3 are taken into account. Additionally, the volume-weighted concentration can readily be converted into total deposition by multiplying by the accumulated precipitation over the time period of interest.

The lowest recorded pH value from the period 1983-1989 was 2.95 at the Rough River State Park monitoring site, while the highest value was 7.00 at Columbus-Belmont State Park. The volume-weighted pH for data from all monitoring sites during 1983-1989 was 4.28. The lowest volume-weighted pH (4.19) for the entire period was obtained at Kincaid Lake State Park in northeastern Kentucky and the highest volume-weighted pH (4.41) was obtained at Columbus-Belmont State Park in far western Kentucky. Generally higher volume-weighted pH values occurred in western Kentucky while lower values occurred toward the northeast, indicating an increasing gradient of acidity across the state from the southwest to the northeast. A similar spatial gradient was observed for volume-weighted concentrations of both $SO_4^=$ and NO_3^- ; the highest volume-weighted concentrations for these species again occurred at Kincaid Lake State Park, and the lowest values occurred at Columbus-Belmont State Park. No statewide spatial gradients of any other measured chemical species were observed during the period.

3.2 Seasonal patterns

Seasonal patterns of precipitation chemistry from the KADP network are illustrated in Figure 4. Shown there are monthly precipitation totals and volume-weighted H^+, $SO_4^=$, and NO_3^- concentrations at the Lexington monitoring station for 1987, which are representative of the seasonal behavior of most sites in the network. Concentrations of $SO_4^=$ and H^+ are typically highest during the warm months of April through September, while generally lower concentrations prevail during the cooler months of October through March. This behavior has been reported in other studies (Raynor and Hayes, 1982; Lindberg, 1982; Pratt and Krupa, 1983; Dasch and Cadle, 1985; and Khwaja and Husain, 1990) and is likely due, at least in part, to the increased oxidation rate of SO_2 at warmer temperatures and possibly higher SO_2 emissions during these months. In addition, long periods of stagnant air occur frequently during summer on the North American continent; sudden downpours from thunderstorms then wash out the accumulated pollutants resulting in relatively high ion concentrations in rainwater.

The seasonal variation of NO_3^- concentrations is not as systematic as that of $SO_4^=$ or H^+. In fact, considering data from the entire network, only a weak seasonal pattern emerges with higher NO_3^- values more likely during warmer months. This result is different from that obtained by some researchers who report an increase in NO_3^- concentrations during winter due to better capture efficiency by snowflakes (Raynor and Hayes, 1982 and Topol, 1986).

Figure 5 shows the monthly behavior of the soil derived components Ca^{++}, Mg^{++}, and K^+ at Lexington for 1987. As seen in Figure 4(a), the months of August, September, and October were very dry at Lexington during 1987. For these dry months, the soil derived ions show a sharp increase in concentration, reflecting the increased amount of dust suspended in the lower atmosphere. At the same time, $SO_4^=$ and NO_3^- concentrations are at their highest levels while H^+ values are not comparably elevated, presumably because much of the acidity has been neutralized by alkaline soil-derived substances.

An interesting seasonal behavior for NH_4^+ concentrations is illustrated in Figure 6, where volume-weighted monthly values for the Perryville site are plotted for 1985. Each year a distinct NH_4^+ concentration maximum occurs during the spring months of March through June. Since the major sources of NH_3 emissions are known to be animal wastes and fertilizers (Buijsman et al., 1987), the maximum in NH_4^+ concentrations may be the result of early spring fertilization at local agricultural sites. NH_3 is an important constituent in precipitation since it can act as an acid neutralizing agent. Since it acts to increase precipitation pH, NH_3 also plays a significant role in the uptake of sulfur dioxide, which is more readily absorbed into cloud and rain drops at higher pH.

3.3 Ionic species relationships

Ion pair correlation coefficients are shown in Table 4 for the entire KADP data set from 1983 through 1989. The highest correlations appear for the ion pairs $SO_4^=$ and NO_3^- ($r = 0.82$), Ca^{++} and NO_3^- ($r = 0.77$), NH_4^+ and NO_3^- ($r = 0.67$), NH_4^+ and $SO_4^=$ ($r = 0.66$), H^+ and $SO_4^=$ ($r = 0.65$), H^+ and Cl^- ($r = 0.65$), and Ca^{++} and $SO_4^=$ ($r = 0.64$). Other relatively high correlations include Ca^{++} and NH_4^+ ($r = 0.59$), H^+ and NO_3^- ($r = 0.53$), and Mg^{++} and Ca^{++} ($r = 0.52$). Most of these well correlated pairs have common sources or occur in precipitation as a result of a common source or compound; e.g., $Ca(NO_3)_2$, $CaSO_4$, H_2SO_4 , HNO_3 , $(NH_4)_2SO_4$, NH_4NO_3 , etc. The ion pair Mg^{++} and Ca^{++} is probably well correlated due to the common occurrence of these species in dusts and soil derived compounds, while $SO_4^=$ and NO_3^- are probably correlated due to the coemission of their direct precursors, SO_2 and NO_x , from fossil fuel combustion sources. The relatively high correlations of NH_4^+ and NO_3^- and NH_4^+ and $SO_4^=$ apparently stem from the neutralization of sulfuric and nitric acids by dissolved NH_3. Likewise, the correlations of Ca^{++} with $SO_4^=$ and NO_3^- also probably result from the neutralization of these acids by alkaline soil compounds containing Ca^{++}, indicating that wind carried dust and soil play a significant role in precipitation chemistry (Applin and Jersak, 1986; Munger, 1982).

Multiple regression analyses were performed on the KADP data set in order to identify which ions contribute most to precipitation acidity. The analyses were performed with H^+ as the dependent variable and the other ion concentrations as independent variables using the SAS procedure STEPWISE (SAS, 1985). Table 5 presents the best-fit results as determined by STEPWISE for the entire data set as well as for each individual site over the entire 1983-1989 period. These results indicate that Cl^- and $SO_4^=$ ions are most closely correlated with precipitation acidity with NO_3^- playing a significant but slightly weaker role. Although the regression coefficients of Cl^- are higher than those for $SO_4^=$, HCl probably plays a minor role in precipitation acidification since average concentrations of Cl^- are only one-fifth as large as average $SO_4^=$ concentrations. As would be expected, ions typically associated with alkaline substances (Ca^{++}, Mg^{++}, K^+, and NH_4^+) are present in the regression equations with negative coefficients indicating that they act to decrease precipitation acidity.

If the trace species composition of precipitation was solely the result of dissolved sulfuric and nitric acids, the correlation of ($SO_4^= + NO_3^-$) with H^+ would approach unity

1). As presented in Table 6 and shown in Figure 7, however, other trace species are important in the actual overall anion-cation balance. The correlation coefficient for ($SO_4^=$ + NO_3^-) versus H^+ is only 0.64, while the addition of Cl^- to the anion sum raises the correlation to 0.75, again implying that hydrochloric acid may be contributing somewhat to total precipitation acidity. Even higher anion/cation correlations are obtained when NH_4^+ and Ca^{++} are added to H^+, thereby indicating that not all of the $SO_4^=$ and NO_3^- in precipitation is necessarily associated with H_2SO_4 and HNO_3, but may also occur in combination with NH_4^+ or Ca^{++}.

3.4 Annual Deposition Variability

One of the major uses of data from a precipitation chemistry network is to evaluate the temporal trend of chemical deposition. Increasing magnitudes of chemical deposition to terrestrial surfaces and ecosystems are likely to be considered objectionable and may lead to greater emission control efforts, while decreasing deposition magnitudes will be expected as more stringent control measures are put in place. Since the KADP precipitation chemistry network has been in operation for only six years, 1984-1989 (one site, PB, was initiated in December 1983), truly long-term trends cannot yet be definitively discerned due to the influence of normal meteorological variability. However, even though a quantitative time series analysis is not justified for such a short span of time, it is desirable to at least obtain an initial qualitative estimate of annual deposition trends.

Figure 8 presents a summary of total annual deposition amounts for $SO_4^=$, NO_3^-, Cl^-, NH_4^+, Ca^{++}, and H^+ for combined data from all sites in the KADP network. Due to the fact that many of the monitoring sites were initiated in 1984 and therefore have only partially complete data for that year, only depositions for 1985 through 1989 are presented in Figure 8. No significant qualitative temporal trends are readily apparent in any of the species depositions. Depositions for $SO_4^=$, NO_3^-, and NH_4^+ all were at their highest levels in 1989, but generally exhibit no clearly increasing trend over the 1985-1989 period. Deposition amounts for Cl^-, Ca^{++}, and H^+ are relatively constant during this period. One of the main objectives for the KADP network over the coming years will be to continue monitoring deposition trends in the lower Ohio River valley.

4. Conclusions

Data from the Kentucky Acid Deposition Program Precipitation Chemistry Network for the period 1983-1989 have been analyzed to characterize the chemical composition of precipitation in the lower Ohio River valley. The major conclusions from the present analysis are:

1. H_2SO_4 and HNO_3 seem to be the primary contributors to precipitation acidity in this region; HCl seems to contribute somewhat but probably plays only a secondary role.

2. Alkaline soil dust compounds containing Ca^{++}, Mg^{++}, and K^+ contribute significantly to the neutralization of precipitation acidity; NH_3 also seems to play a major role in the neutralization process.

3. H^+, $SO_4^=$, and NO_3^- ions exhibit a seasonal pattern in which higher precipitation concentrations occur in summer and lower concentrations occur in winter. Observations of the prevailing atmospheric conditions at the time of largest ionic concentrations indicate that these large concentrations are the result of below-cloud rainout of acidic aerosols after an extended period of dryness and air stagnation.

4. NH_4^+ concentrations in precipitation exhibit a seasonal pattern in which higher values occur in spring, possibly as a result of increases in local agricultural activity.

5. Total annual depositions of $SO_4^=$, NO_3^-, Cl^-, NH_4^+, Ca^{++}, and H^+ show no apparent qualitative temporal trend from 1985 through 1989 in this region.

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Table 1. The Kentucky Acid Deposition Program Precipitation Chemistry Network Monitoring Stations

Site	Start Date	County	Latitude *	Longitude *	Elevation (mASL)
Barren River State Park(BR)	March 1984	Barren	36:51:30 N	86:03:16 W	213
Columbus-Belmont State Park (CB)	Dec. 1985	Hickman	36:45:45 N	89:06:30 W	134
Dewey Dam State Park(DD)	July 1984	Floyd	37:44:30 N	82:43:47 W	220
Hope Creek (HC)	August 1985	Montgomery	38:00:43 N	83:48:10 W	305
J. J. Audubon State Park (JA)	May 1986	Henderson	37:52:32 N	87:33:07 W	171
Kincaid Lake State Park (KL)	March 1985	Pendleton	38:43:07 N	84:17:15 W	222
Lexington-UKCAER (LX)	January 1984	Fayette	38:08:18 N	84:30:55 W	262
Perryville Battlefield State Park (PB)	Dec. 1983	Boyle	37:40:29 N	84:58:32 W	281
Pine Mountain State Park (PM)	August 1984	Bell	36:43:15 N	83:41:58 W	347
Rough River State Park (RR)	Sept. 1984	Grayson	37:36:27 N	86:30:20 W	175

* degrees:minutes:seconds

Table 2: Chemical Species and Analytical Methods

Species	Method *	Instrument	MDL **
Conductivity	electrode	YSI model 32 Conductance Meter with YSI model 3403 conductivity cell	--
H^+	electrode	Orion Research model 901 pH Meter with Orion-Ross pH electrode	--
$SO_4^=$	IC	Dionex System 2020i (anion column)	0.6
NO_3^-	IC	Dionex System 2020i (anion column)	0.5
Cl^-	IC	Dionex System 2020i (anion column)	0.8
Na^+	IC	Dionex System 2020i (cation column)	1.3
K^+	IC	Dionex System 2020i (cation column)	0.8
Ca^{++}	ICP	Plasma-Therm ICP 2500	0.5
Mg^{++}	ICP	Plasma-Therm ICP 2500	0.8
NH_4^+	IC	Dionex System 2020i (cation column)	1.7

* IC = ion chromatography; ICP = inductively coupled plasma emission spectroscopy

** minimum detection limit (microequivalents/liter)

Table 3: Statistical Summary for the Kentucky Acid Deposition Program Precipitation Chemistry Network 1983-1989

							(microequivalents/liter)					
Site		Precipitation(cm)	Conductivity microS/cm	$SO_4^{=}$	NO_3^-	Cl^-	H^+	Na^+	K^+	Ca^{++}	Mg^{++}	NH_4^+
	Min	0.04	5.2	MDL	0.8	MDL	0.3	MDL	MDL	MDL	MDL	MDL
BR	Max	30.4	183.5	383.9	487.6	213.6	416.9	213.6	81.4	494.1	74.8	133.3
n=182	A.Mean	3.0	36.3	77.6	38.2	17.6	65.6	9.6	2.4	26.4	6.5	18.0
	G.Mean	–	–	57.9	25.8	10.8	49.1	6.2	0.9	11.4	2.8	12.3
	V.W.Mean	–	–	56.6	24.5	10.2	47.6	6.8	0.9	12.5	3.9	14.6
	Min	0.08	0.5	12.4	5.2	1.6	0.1	MDL	MDL	1.2	MDL	MDL
CB	Max	17.1	225.6	366.0	170.5	183.9	436.5	70.7	25.9	406.9	311.0	136.1
n=141	A.Mean	2.6	30.9	56.4	26.3	20.7	55.4	9.6	2.3	18.6	6.4	17.5
	G.Mean	–	–	43.5	22.6	11.0	35.2	8.5	1.4	8.7	2.2	11.6
	V.W.Mean	–	–	40.1	18.5	12.4	39.2	6.5	1.6	8.4	2.0	12.9
	Min	0.06	4.1	7.6	2.6	1.0	1.6	MDL	MDL	MDL	MDL	MDL
DD	Max	13.6	255.1	644.0	283.2	107.0	681.6	58.2	35.1	643.9	83.8	222.2
n=205	A.Mean	2.1	37.3	65.4	38.1	12.3	68.9	8.2	1.7	24.4	4.9	23.5
	G.Mean	–	–	64.0	28.9	8.5	52.1	5.3	0.9	10.5	2.0	13.2
	V.W.Mean	–	–	62.5	25.8	7.6	58.0	6.4	1.0	9.5	2.1	13.2
	Min	0.08	6.6	5.1	2.9	1.6	10.5	MDL	MDL	MDL	MDL	MDL
HC	Max	16.0	332.6	335.2	167.6	574.9	681.9	50.2	284.2	272.0	51.0	426.7
n=81	A.Mean	2.1	44.4	77.4	38.8	22.0	86.6	7.5	5.3	17.6	3.6	24.9
	G.Mean	–	–	81.1	31.1	10.2	83.9	5.7	0.6	10.0	2.0	13.3
	V.W.Mean	–	–	54.0	24.0	6.9	55.7	4.6	2.0	6.4	2.2	14.4
	Min	0.03	6.7	8.5	4.2	1.6	9.3	1.8	MDL	MDL	MDL	MDL
JA	Max	6.5	386.6	388.6	181.9	190.6	851.1	66.6	10.7	244.6	60.9	88.0
n=65	A.Mean	2.6	41.0	66.9	39.0	15.6	76.1	9.6	1.6	28.6	5.9	25.0
	G.Mean	–	–	69.2	28.9	9.7	53.2	6.2	0.6	13.1	2.4	18.7
	V.W.Mean	–	–	67.2	25.9	9.7	57.7	6.0	0.9	12.0	2.3	18.1
	Min	0.03	5.0	MDL	2.1	1.5	0.9	MDL	MDL	MDL	MDL	MDL
KL	Max	10.5	186.3	583.3	217.3	107.9	331.1	63.9	10.3	175.7	42.0	105.5
n=217	A.Mean	2.2	39.3	65.9	37.9	11.0	79.9	6.4	1.0	15.6	4.0	20.1
	G.Mean	–	–	66.2	28.6	6.4	63.9	4.6	0.5	7.9	2.0	13.7
	V.W.Mean	–	–	66.6	27.9	7.9	65.1	4.9	0.7	9.0	2.6	16.0
	Min	0.06	6.6	7.7	4.4	1.3	0.1	MDL	MDL	MDL	MDL	MDL
LX	Max	10.9	157.6	407.2	244.5	50.9	257.0	78.6	43.6	369.3	75.7	266.9
n=210	A.Mean	2.2	35.1	85.0	37.7	7.9	64.2	6.2	1.6	21.4	4.5	31.0
	G.Mean	–	–	69.7	28.7	8.5	49.1	4.3	0.7	12.1	2.3	21.6
	V.W.Mean	–	–	69.4	26.6	6.7	56.2	5.3	1.2	11.7	2.5	22.7
	Min	0.03	3.4	MDL	0.9	1.1	0.5	MDL	MDL	0.6	MDL	MDL
PS	Max	19.7	613.7	2084	731.7	134.3	833.2	61.9	11.5	556.0	234.5	318.4
n=253	A.Mean	2.4	32.9	73.2	33.0	7.5	58.0	6.0	1.0	14.9	4.6	18.1
	G.Mean	–	–	51.9	23.1	5.1	40.7	3.7	0.5	7.9	2.4	10.2
	V.W.Mean	–	–	47.3	18.0	4.3	42.3	3.3	0.6	6.6	1.6	12.2
	Min	0.05	7.0	12.6	MDL	2.3	4.9	MDL	MDL	MDL	MDL	MDL
PM	Max	10.6	421.2	343.9	198.4	838.2	1000	33.6	40.2	167.7	37.6	126.7
n=114	A.Mean	2.5	36.0	78.2	33.4	18.6	72.9	6.9	2.9	22.1	6.1	16.4
	G.Mean	–	–	64.2	26.3	9.4	54.1	5.0	1.2	13.2	3.6	10.3
	V.W.Mean	–	–	57.2	24.4	9.1	50.0	5.5	2.0	12.5	4.3	11.6
	Min	0.04	7.1	12.2	1.6	1.6	0.5	MDL	MDL	MDL	MDL	MDL
RR	Max	15.2	474.1	306.3	177.6	872.6	1122	51.3	85.3	248.4	515.0	163.6
n=182	A.Mean	2.7	35.1	72.4	32.0	18.2	67.9	7.9	2.4	18.2	7.9	18.2
	G.Mean	–	–	60.6	24.6	9.3	47.5	5.5	0.9	10.3	2.3	12.2
	V.W.Mean	–	–	54.2	20.4	11.3	56.6	5.9	1.9	6.5	4.5	13.4

MDL = < minimum detection limit

Table 4: Ion Pair Correlations . . . 1983-1989

N = 1670

	Cl^-	NO_3^-	$SO_4^=$	Na^+	K^+	Ca^{++}	Mg^{++}	NH_4^+	H^+
Cl^-	1.00								
NO_3^-	0.29	1.00							
$SO_4^=$	0.25	0.82	1.00						
Na^+	0.30	0.47	0.30	1.00					
K^+	0.11	0.23	0.16	0.32	1.00				
Ca^{++}	0.30	0.77	0.64	0.57	0.25	1.00			
Mg^{++}	0.26	0.38	0.36	0.33	0.11	0.52	1.00		
NH_4^+	0.14	0.67	0.66	0.36	0.46	0.59	0.29	1.00	
H^+	0.65	0.53	0.65	0.11	0.03	0.29	0.14	0.31	1.00

Table 5: Multiple Regression Best-Fit Models

Site	a	b	c	d	e	f	g	h	i	s	r^2
All	15.7	1.17	0.36	0.62	-0.93	-0.18	-0.53	-0.45	-0.22	34.0	0.79
BR	17.8	1.10	0.25	0.64	-1.15		-0.49	-1.00		35.8	0.64
CB	-1.1	1.18	0.97	0.73	-0.83	-0.82	-0.65		-0.84	20.2	0.90
DD	2.2	3.29	0.70	0.51	-0.87		-0.72		-0.83	36.3	0.72
HC	-2.4	0.70	0.96	0.98		0.57	-1.29		-0.75	34.3	0.87
JA	-6.6	3.60	0.35	0.70	-1.37	-8.62		-3.96		26.6	0.94
KL	13.4	1.32	0.53	0.70	-1.81	-4.43	-0.77			27.3	0.79
LX	9.5	-1.39	0.36	0.84			-0.50		-0.36	15.7	0.89
PB	2.5	0.56	0.80	0.79	0.35	-3.37	-0.64	-3.79	-0.20	15.3	0.95
PM	14.6	1.09		0.78	-0.76	-1.19		-1.10	-0.56	20.2	0.96
RR	8.1	1.13	0.54	0.82	-0.80	-0.84	-0.64	-0.38	-0.70	36.4	0.86

Regression Equation: (concentrations in microequivalents/liter)

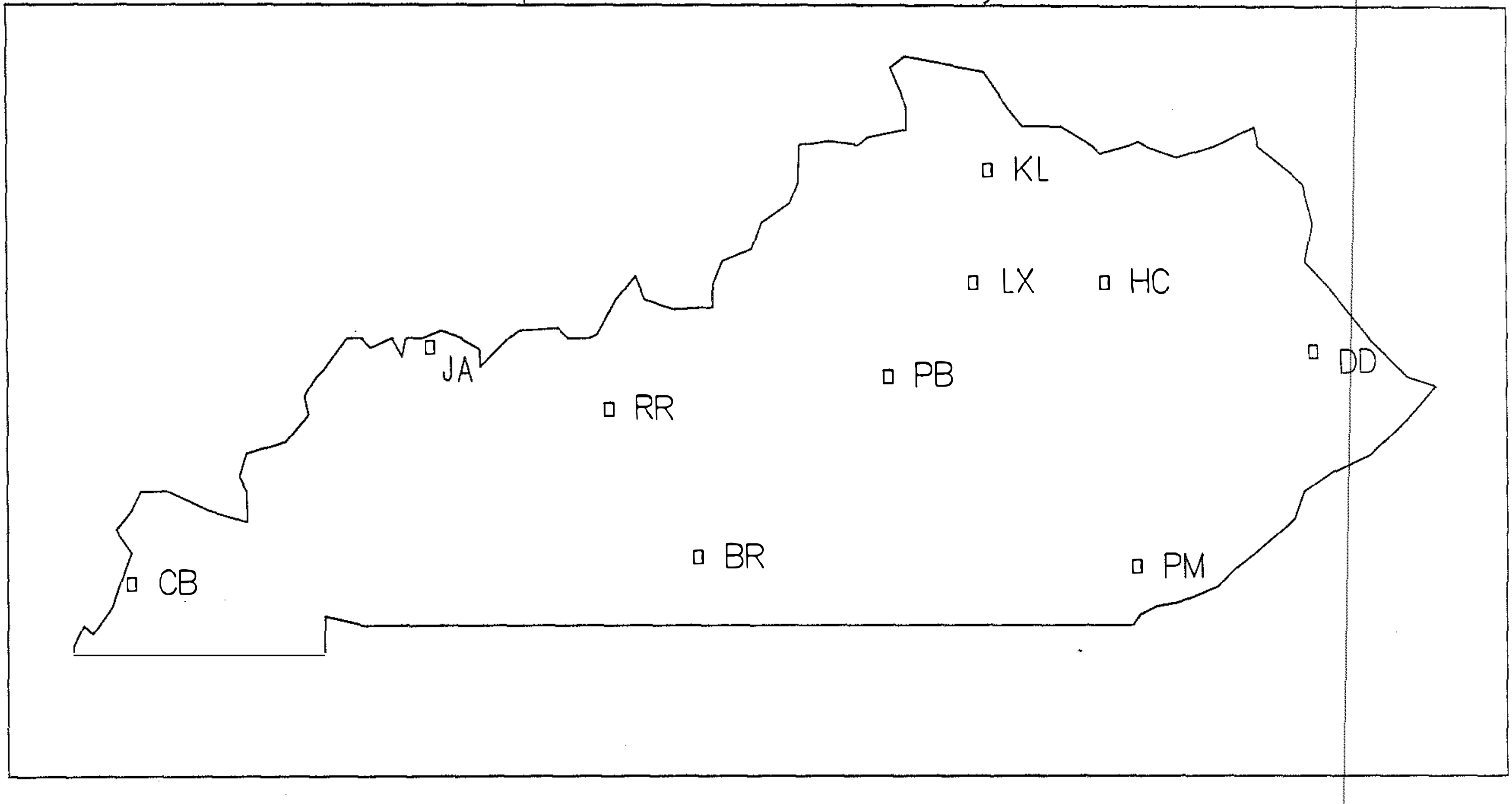
$$[H^+] = a + b[Cl^-] + c[NO_3^-] + d[SO_4^=] + e[Na^+] + f[K^+] + g[Ca^{++}] + h[Mg^{++}] + i[NH_4^+]$$

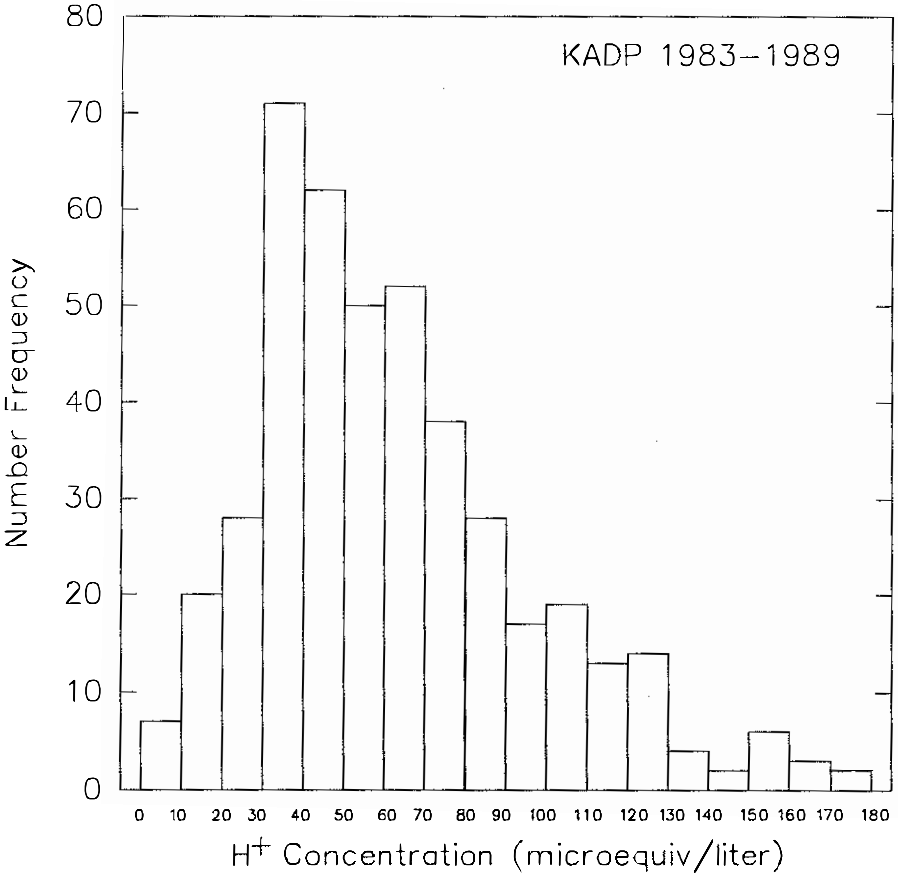
s = Root Mean Square Error
r = Correlation Coefficient

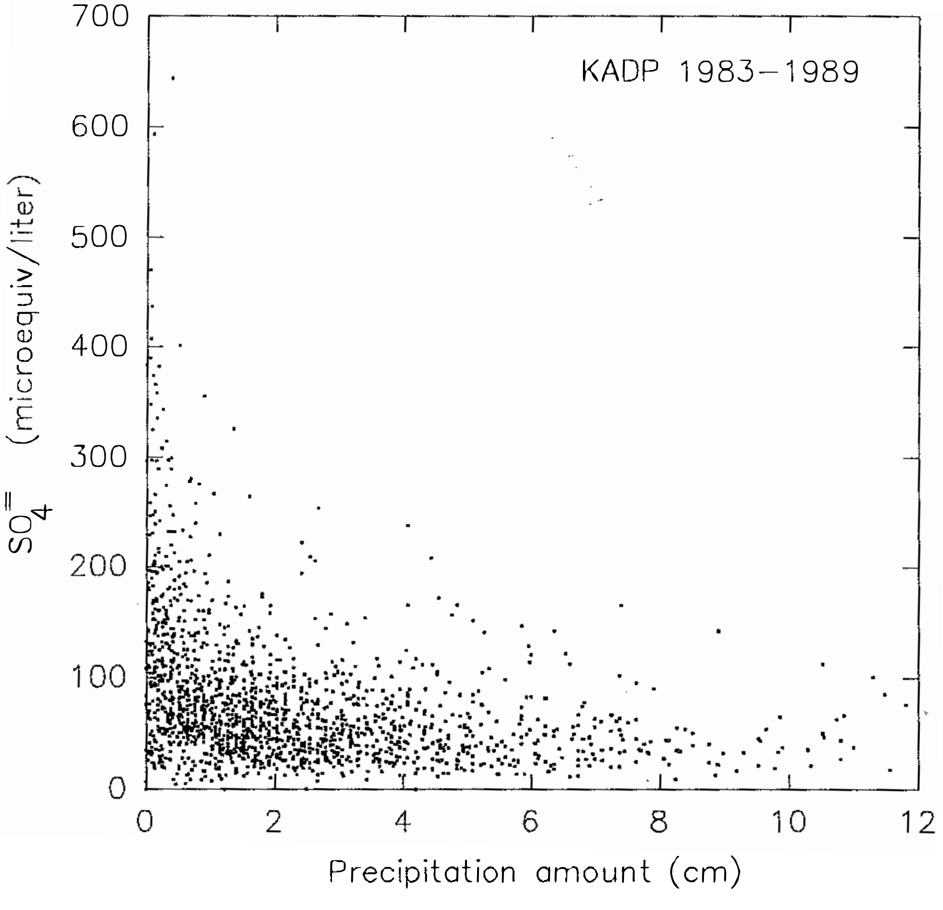
Table 6: Correlation Coefficients for Anion vs. Cation Combinations

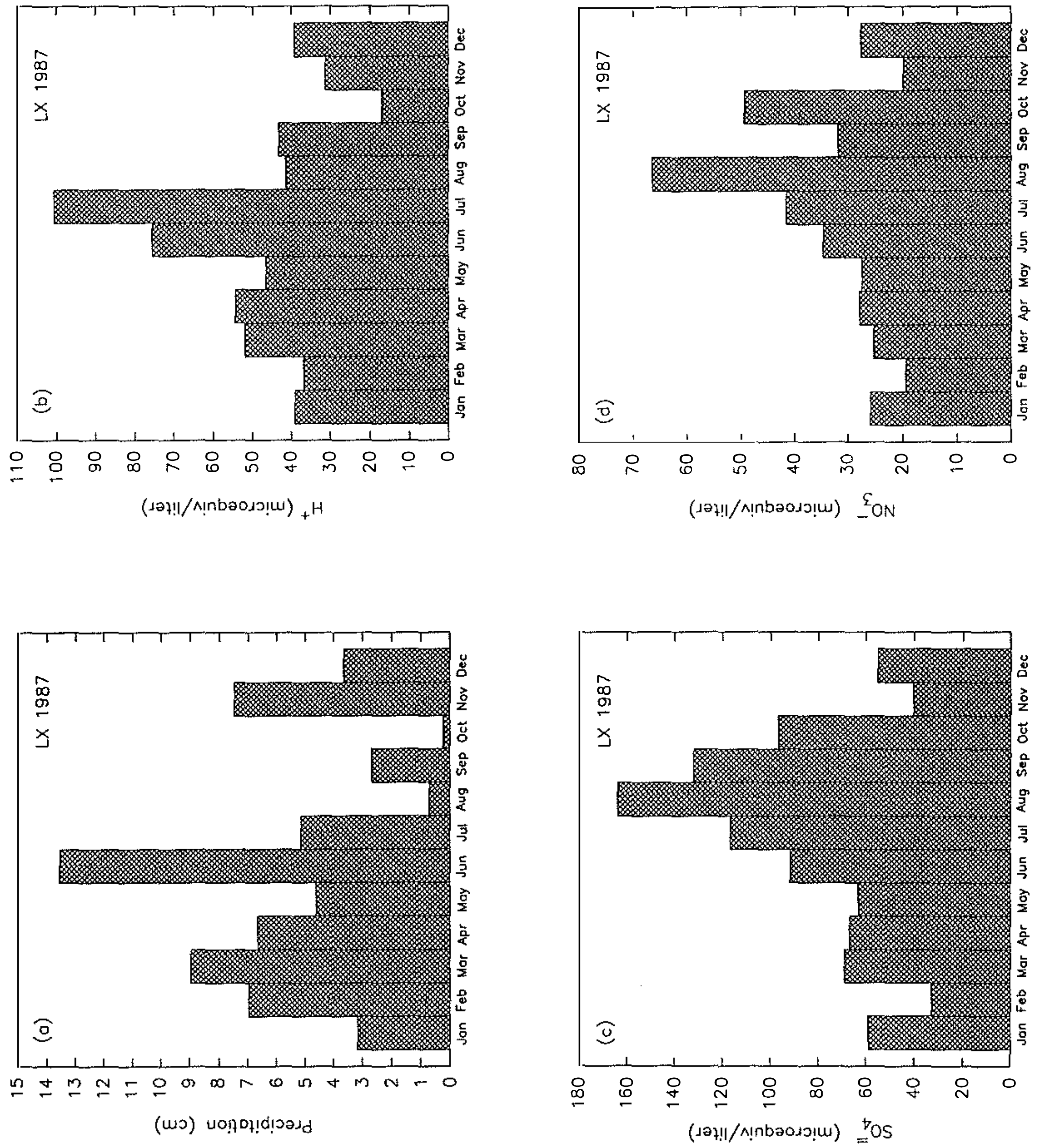
$(SO_4^{=} + NO_3^{-})$	0.64	0.76	0.86
$(SO_4^{=} + NO_3^{-} + Cl^{-})$	0.75	0.84	0.93
	H^{+}	$(H^{+} + NH_4^{+})$	$(H^{+} + NH_4^{+} + Ca^{++})$

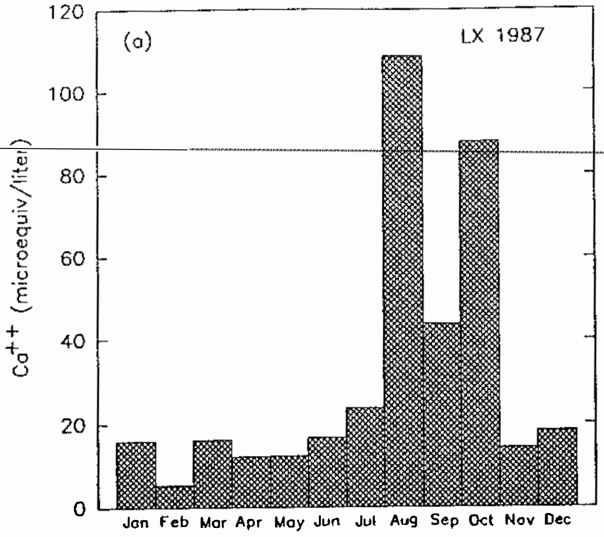
KADP Precipitation Chemistry Network



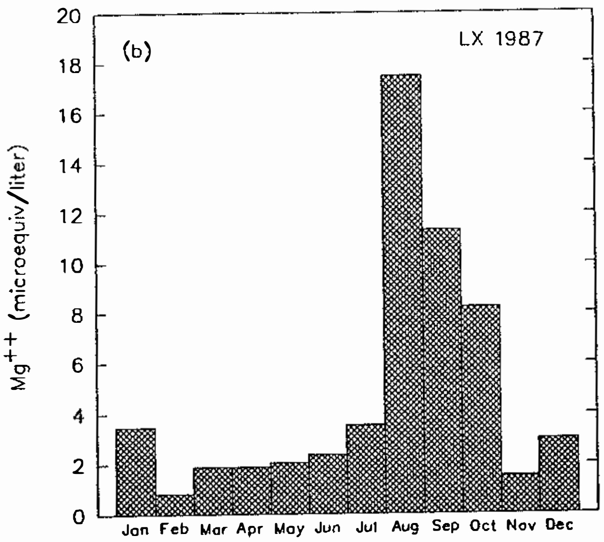

KADP 1983–1989
Number Frequency
0
10
20
30
40
50
60
70
80
0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180
H^+ Concentration (microequiv/liter)


KADP 1983–1989
$SO_4^{=}$ (microequiv/liter)
700
600
500
400
300
200
100
0
0
2
4
6
8
10
12
Precipitation amount (cm)

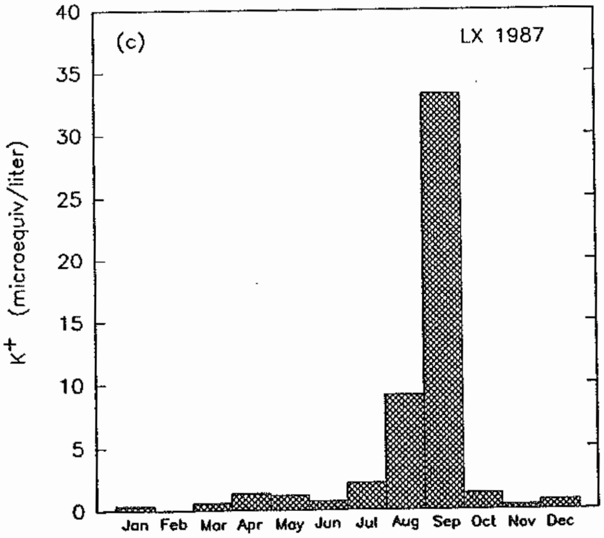

(a)
LX 1987
Precipitation (cm)
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec
(b)
LX 1987
H^+ (microequiv/liter)
0
10
20
30
40
50
60
70
80
90
100
110
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec
(c)
LX 1987
$SO_4^=$ (microequiv/liter)
0
20
40
60
80
100
120
140
160
180
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec
(d)
LX 1987
NO_3^- (microequiv/liter)
0
10
20
30
40
50
60
70
80
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec



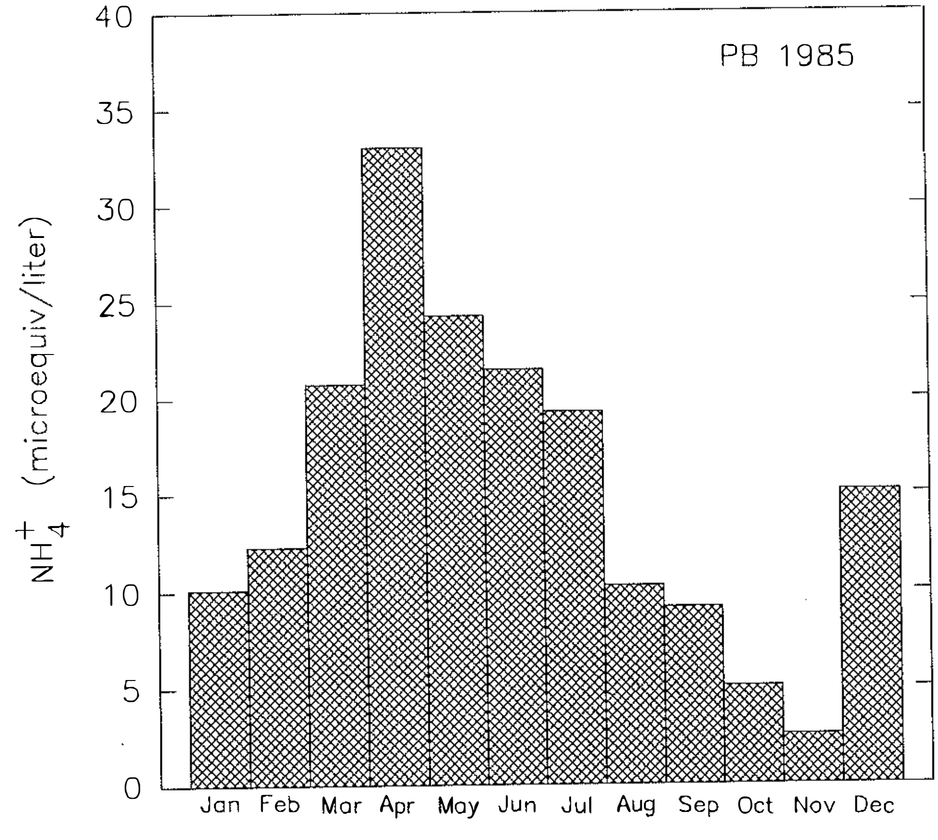
(a)
LX 1987
Ca^{++} (microequiv/liter)
0
20
40
60
80
100
120
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec



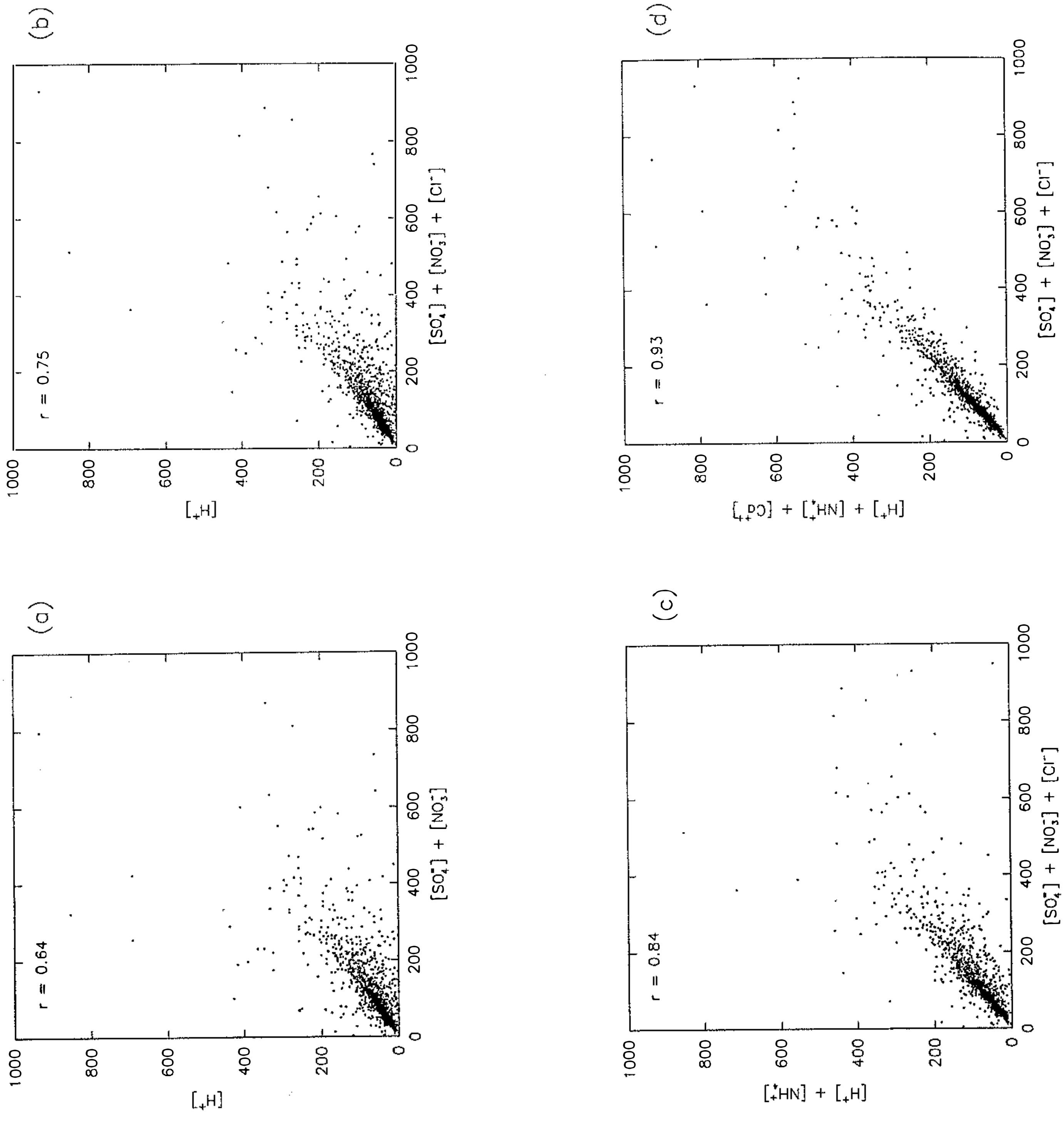
(b)
LX 1987
Mg^{++} (microequiv/liter)
0
2
4
6
8
10
12
14
16
18
20
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

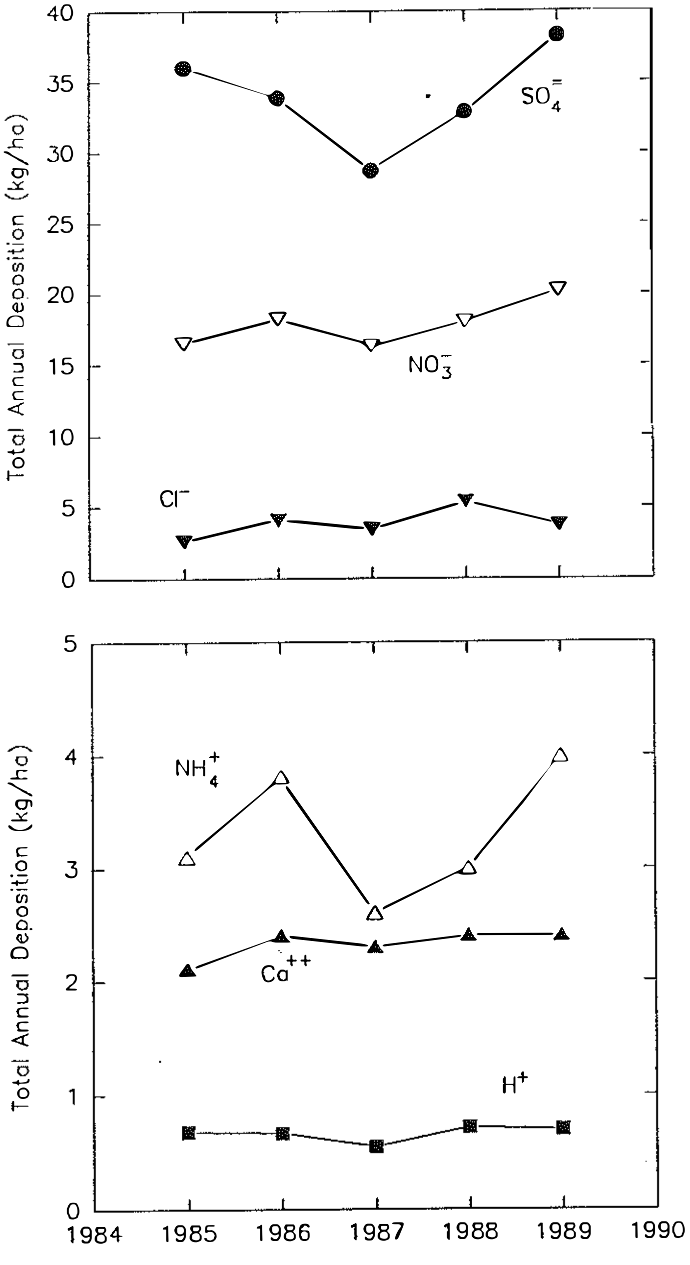


(c)
LX 1987
K^{+} (microequiv/liter)
0
5
10
15
20
25
30
35
40
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec



PB 1985
NH_4^+ (microequiv/liter)
0
5
10
15
20
25
30
35
40
Jan
Feb
Mar
Apr
May
Jun
Jul
Aug
Sep
Oct
Nov
Dec


(a)
r = 0.64
[H+]
[SO4=] + [NO3-]
(b)
r = 0.75
[H+]
[SO4=] + [NO3-] + [Cl-]
(c)
r = 0.84
[H+] + [NH4+]
[SO4=] + [NO3-] + [Cl-]
(d)
r = 0.93
[H+] + [NH4+] + [Ca++]
[SO4=] + [NO3-] + [Cl-]
0
200
400
600
800
1000



Total Annual Deposition (kg/ha)
40
35
30
25
20
15
10
5
0
$SO_4^=$
NO_3^-
Cl^-
Total Annual Deposition (kg/ha)
5
4
3
2
1
0
NH_4^+
Ca^{++}
H^+
1984
1985
1986
1987
1988
1989
1990