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Comparison of Process Aid Ingredients In A Water-Resistant Neoprene

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James L. Merryfield

*Underwater Sound Reference Detachment
Naval Research Laboratory
P.O. Box 568337
Orlando, FL 32856-8337*

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13. ABSTRACT (Maximum 200 words) Neoprene compound 5109 is used extensively by the NRL-USRD and industrial activities for underwater acoustical devices. It contains a proprietary process aid (Technical Processing, Inc. TE-70). Recently, TE-70 has become very difficult for the NRL-USRD to obtain. This report outlines work by the NRL-USRD to eliminate use of proprietary materials in the formulation of compound 5109. Two approaches are presented: (1) Eliminate the use of any process aid; (2) Reformulate compound 5109 using alternative process aids. This report also describes the processability, physical characteristics, and bondability of several alternative formulations for Neoprene 5109.			
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CONTENTS

INTRODUCTION..... 1

FORMULATION CHARACTERIZATICS..... 1

PROCESSABILITY AND PHYSICAL TESTING..... 5

Cathodic Delamination Tests..... 6

Deionized Water Delamination Tests..... 7

CONCLUSIONS..... 7

REFERENCES.....18

ACKNOWLEDGMENTS.....18

APPENDIX - Materials List.....19

FIGURES

Fig.

1 Adhesion Test, Run 1, Cathodic Delamination Test..... 9

2 Adhesion Test, Run 1A, Cathodic Delamination Test.....10

3 Adhesion Test, Run 1, Deionized Water Test.....11

4 Adhesion Test, Run 1, % Adhesion Retained Test.....12

5 Adhesion Test, Run 2, Cathodic Delamination Test.....13

6 Adhesion Test, Run 2.1, Cathodic Delamination Test.....14

7 Adhesion Test, Run 2.4, Cathodic Delamination Test.....15

8 Adhesion Test, Run 2, Deionized Water Test.....16

9 Adhesion Test, Run 2, % Adhesion Retained Test.....17

TABLE

Table

1 Candidate Formulations.....2-5



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COMPARISON OF PROCESS AID INGREDIENTS IN A WATER RESISTANT NEOPRENE

INTRODUCTION

Neoprene compound 5109 is an uncomplicated formulation designed for long-term exposure in water, including applications where rubber-to-metal bonding is important. It has been studied extensively at the Naval Research Laboratory's Underwater Sound Reference Detachment (USRD) in Orlando, FL, and has had several years in-the-field service. This formulation is particularly useful for underwater acoustical applications typically encountered at the NRL-USRD.

One of the ingredients in Neoprene 5109 is a proprietary process aid, TE-70. Unfortunately, this material has become difficult for the USRD to obtain. What historically has been an easily reproducible formulation is now a problem.

Our objective was to minimally modify the Neoprene 5109 compound with the goal of independence from single source proprietary ingredients.

Two approaches were explored:

- Eliminate the use of any process aid.
- Reformulate the Neoprene 5109 compound using alternative process aids.

This report summarizes the work done on both approaches. Candidate compounds were evaluated based on their processability, physical properties, and bonding characteristics.

FORMULATION CHARACTERISTICS

The most important criterion for a stock to become a candidate for adhesion study is that its properties not deviate significantly from the original Neoprene 5109 compound. Four important characteristics are:

- Modulus at 100% and 300%
- Compression set
- Minimum torque (rheometer value)
- Time to two point rise (rheometer value)

J.L. Merryfield

These processability and physical tests were done in accordance with ASTM specifications [1].

- ASTM D-3182 Preparation of vulcanized sheets
- ASTM D-412 Tensile, elongation and modulus
- ASTM D-395 Compression set method B
- ASTM D-2240 Durometer hardness
- ASTM D-2084 Rheometer vulcanization characteristics

The rheometer measures rate and state of cure for its unique test specimens; these have identical volume and shape. Direct comparison of data that is obtained from these identical samples is meaningful. However, for articles with different volume and shape, cure times have to be determined experimentally. This is especially true for products that are irregularly shaped, very thick, or have a metal insert.

A total of 13 formulations were studied, including two controls. Compound samples were assigned letters from A to M which were appended to the series number 89-1 (e.g., 89-1-A, 89-1-B, etc).

Compound 89-1-A contained no process aid and served as a control as well as a candidate. Compound 89-1-B is formulated with process aid TE-70, which is the usual formulation for Neoprene 5109 and served as the primary control. Compounds 89-1-C through 89-1-M contained additives or modifications that are compared to the controls.

Table 1 summarizes the formulations and test results. A description of the various tests and conclusions is also presented.

Table 1 - Candidate Formulations

<u>Series 89-1-</u>	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>	<u>E</u>	<u>F</u>
Neoprene GRT	100.0	100.0	100.0	100.0	100.0	100.0
Stearic Acid	1.0	1.0	1.0	1.0	1.0	1.0
Octylated diphenylamine	2.0	2.0	2.0	2.0	2.0	2.0
MBTS	1.5	1.5	1.5	1.5	1.5	1.5
90% Red Lead Disp.	15.0	15.0	15.0	15.0	15.0	15.0
N-550 Carbon Black	40.0	40.0	40.0	40.0	40.0	40.0
TE-70		2.0				
W-34			2.0			
WB-222				2.0		
ZO-9					2.0	
Polyethylene (approx. mol. wt. 8,000)						2.0
Total Compound Wt.	159.5	161.5	161.5	161.5	161.5	161.5

Table 1 - (Continued)

Physical Properties - Cured 30 min. at 155°C

100% Modulus	515	415	522	481	496	551
300% Modulus	2175	1863	1881	2004	2097	2065
Tensile (psi)	3278	3149	2998	2920	3226	3013
Elongation (%)	520	570	540	520	540	510
Durometer ("A")	72	70	71	73	73	73
Compression set (%)	78	70	77	79	81	83

Physical Properties - Cured 60 min. at 155°C

100% Modulus	565	452	522	481	496	551
300% Modulus	2283	2204	2114	2061	2148	2259
Tensile (psi)	3109	3278	3074	3029	3052	3147
Elongation (%)	460	500	480	470	470	460
Durometer ("A")	71	70	74	71	72	73
Compression Set %	51	49	55	55	56	54

Rheometer Data at 155°C:

ML (Torque Units)	14.75	8.00	10.25	9.50	11.00	16.75
MH (Torque Units)	82.0	71.0	73.0	71.5	76.5	82.0
Minutes to 2-point rise or Scorch Time	3.00	2.88	2.63	3.38	2.69	3.19
Minutes to 10-pt rise ¹	4.31	4.38	3.62	4.50	4.03	4.38
Minutes to 90% cure	20.43	21.19	20.63	20.38	20.25	21.38

Note 1. This value has been used by others in previous reports on Neoprene 5109 characteristics and in some Navy specifications. It is included for comparison purposes.

<u>Series 89-1-</u>	<u>G</u>	<u>H</u>	<u>I</u>	<u>J</u>	<u>K</u>	<u>L</u>
Neoprene GRT	100.0	100.0	100.0	100.0	100.0	100.0
Stearic Acid	1.0	1.0	1.0	1.0	1.0	1.0
Octylated diphenylamine	2.0	2.0	2.0	2.0	2.0	2.0
MBTS	1.5	1.5	1.5	1.5	1.5	1.5
90% Red Lead Disp.	15.0	15.0	15.0	15.0	15.0	15.0
N-550 Carbon Black	40.0	40.0	40.0	40.0	40.0	40.0
Adaphax "758"	2.0	5.0				
Cis 1,4 Polybutadiene			2.0	5.0		
Vanax "552"					0.5	
Vanplast R						2.0
Total Compound Wt.	161.5	164.5	161.5	164.5	160.0	161.5

Table 1 - (Continued)

Physical Properties - Cured 30 min. at 155°C

100% Modulus	515	484	498	565	508	417
300% Modulus	2030	1889	2204	2317	2014	1966
Tensile (psi)	2958	2748	3064	3131	2939	2979
Elongation (%)	500	480	470	480	480	520
Durometer ("A")	72	71	72	72	72	70
Compression Set (%)	87	79	83	78	79	84

Physical Properties - Cured 60 min. at 155°C

100% Modulus	489	501	527	521	498	483
300% Modulus	2154	1903	2370	2275	2155	2114
Tensile (psi)	3106	2746	3223	3236	3155	2899
Elongation (%)	480	450	450	470	500	460
Durometer ("A")	72	74	72	73	71	70
Compression Set (%)	51	51	51	47	56	43

Rheometer Data at 155°C:

ML (Torque Units)	11.25	10.25	16.25	17.00	8.75	10.75
MH (Torque Units)	78.0	70.0	86.5	90.0	73.5	75.25
Minutes to 2-point rise or Scorch Time	3.31	3.31	3.13	3.13	2.38	3.19
Minutes to 10-pt rise ¹	4.56	4.56	4.25	4.25	4.00	4.38
Minutes to 90% cure	19.75	16.43	20.13	19.63	20.43	21.19

Series 89-1-

M

Neoprene GRT	95.0
Neoprene FB	5.0
Stearic Acid	1.0
Octylated diphenylamine	2.0
MBTS	1.5
90% Red Lead Disp.	15.0
N-550 Carbon Black	40.0
Total Compound Wt.	159.5

Physical Properties - Cured 30 min. at 155°C

100% Modulus	502
300% Modulus	2031
Tensile (psi)	2902
Elongation (%)	490
Durometer ("A")	74
Compression Set (%)	84

Table 1 - (Continued)

Physical Properties - Cured 60 min. at 155°C

100% Modulus	575
300% Modulus	2277
Tensile (psi)	3004
Elongation (%)	450
Durometer (°A°)	73
Compression Set (%)	48

Rheometer Data at 155°C

ML (Torque Units)	8.25
MH (Torque Units)	76.0
Minutes to 2-point rise or Scorch Time	3.13
Minutes to 10-pt rise ¹	4.70
Minutes to 90% cure	21.38

PROCESSABILITY AND PHYSICAL TESTING

Adhesion testing was done with stocks chosen because most of their physical and processing characteristics did not deviate significantly from 89-1-B, the control that contained TE-70. All bonding was done to 316 stainless steel. This particular steel was selected because:

1. It is the predominant material used in USRD Standards transducer housings.
2. Stainless steel provides a more severe bonding test than mild steel.
3. A complicating factor, the formation of rust at the bond line, can be avoided by using stainless steel.

Adhesion testing procedures utilized ASTM D-429 [1] specimens and methods but with these two modifications:

1. The bonded area was 1 in. by 2 in. instead of 1 in. by 1 in. to yield a more meaningful distance vs time test in the sodium chloride solution.
2. In the deionized water tests, which utilized a power-driven means of jaw separation, the rate was 20 mm/min. instead of 50 mm/min. to yield a more compact range of results.

One-quarter-in.-thick stainless steel plates were machined to dimensions of 1 in. by 4 in., with attention given to maintaining proper width, flatness of the bonding surface, and squareness of the edges. The plates were degreased, grit blasted, and rinsed with methylethylketone. The two-coat

Chemlok 205/220 bonding system was applied, by brush, according to specifications. The Neoprene stocks were molded to the plates for 60 min at 155°C. Finished assemblies were 6 1/2 in. length bonded to 1 in. by 4 in. stainless steel plates.

Cathodic Delamination Tests

The stocks were divided into two groups for testing convenience.

Group I

- 89-1-A Control/candidate, no additive
- 89-1-B Control, 2 parts TE-70
- 89-1-D 2 parts WB-222
- 89-1-E 2 parts Z0-9
- 89-1-G 2 parts Adaphax 758
- 89-1-M No additive, but a replacement of 5 parts Neoprene GRT with 5 parts Neoprene FB.

Group II

- 89-1-A Control/candidate, no additive
- 89-1-B Control, 2 parts TE-70
- 89-1-C 2 parts W-34
- 89-1-F 2 parts polyethylene
- 89-1-K 0.5 parts Vanax
- 89-1-L 2 parts Vanplast R

All stocks were conditioned in a cathodic delamination tank. This tank is used at the USRD to simulate shipboard conditions [2 and 3]. The tank contained sodium chloride solution of 1.023 specific gravity (the specific gravity of sea water) at a nominal temperature of 23°C. A zinc bar was connected to each adhesion plate so an electro-chemical potential of 1.0 V was established between the zinc bar and the stainless steel plates. In addition, each specimen was stressed with a constant pull of 10 lbs applied evenly across its 1 in. width. This was accomplished by weights and accounted for the buoyant effect of water.

Two Group I cathodic delamination graphs are shown (labeled Run 1 in Fig. 1 and Run 1A in Fig. 2). Group II cathodic delamination tests required a longer time to complete because the tank became inert and delamination slowed almost to a stop. To restore cathodic activity, the tank had to be thoroughly cleaned and the sodium chloride solution replaced. This anomaly did not materially affect adhesion comparisons, but did point out the significant effect of cathodic activity on rubber-to-metal bonding.

For clarity, the Group II cathodic delamination test is shown in three separate graphs. Run 2 (Fig. 5), shows the entire test from 0 to 1368 hrs. This graph shows a marked increase in rate at 892 hrs. due to the inert tank being restored. Figure 6 shows the 0- to 263-hr segment, and Fig. 7 shows the 892- to 1368-hr segment.

Deionized Water Delamination Tests

Both groups were also tested after immersion in deionized water at 60°C for 48 days. This differs from the cathodic delamination tests in several ways:

- There is no electrical potential involved.
- It is a "before and after" test that measures retained adhesion.
- It is an "accelerated" test because of the elevated temperature.
- Deionized water is generally a more severe environment, to rubber, than seawater [4].

The results of these tests for Group I stocks are shown in graphs labeled Run #1 DE-ION (Fig. 3) and Run #1 % Adhesion Retained (Fig. 4). The results for Group II stocks are shown in graphs labeled Run #2 DE-ION (Fig. 8) and Run #2 % Adhesion Retained (Fig. 9).

CONCLUSIONS

Candidate formulations were judged by the following characteristics: modulus, compression set, minimum torque, time to a two point rise and adhesion. The recommended replacement formulations are presented in order of choice.

- Formulation 89-1-A (no process aid)

Formulation 89-1-A has physical properties and processing characteristics that closely resemble the TE-70 formulation. The exception is higher minimum viscosity. This increase may actually enhance processability because viscosity that is too low contributes to trapped air in some molded parts [5].

In each of the four separate adhesion tests, it demonstrated excellent adhesion.

Elimination of the process aid simplifies production and reduces USRD's dependence on proprietary ingredients.

- Formulation 89-1-L (2.0 parts Van plast B)

This material exhibits superior adhesion in all tests.

It shows an increased time to a two-point rise. This demonstrates slightly better processing, safety, and storage stability with respect to control stocks A and B.

The compression set is superior to all other stocks tested.

- **Formulation 89-1-D (2.0 parts WB-222)**

Its adhesion in both Run #1 and Run #1A, sodium chloride water, is the best of Group I and is comparable to the best of Group II.

Its time to a two-point rise is superior to all other stocks tested.

Physical tests and rheometer data indicated that formulations A, L, and D are similar. However, trial runs should be made for specific applications. Verification of the neoprene formulation as used in its final product configuration is highly recommended.

ADHESION: 5109/316 STAINLESS
 10 LB WT; SALT WATER; NOM TEMP 23 C

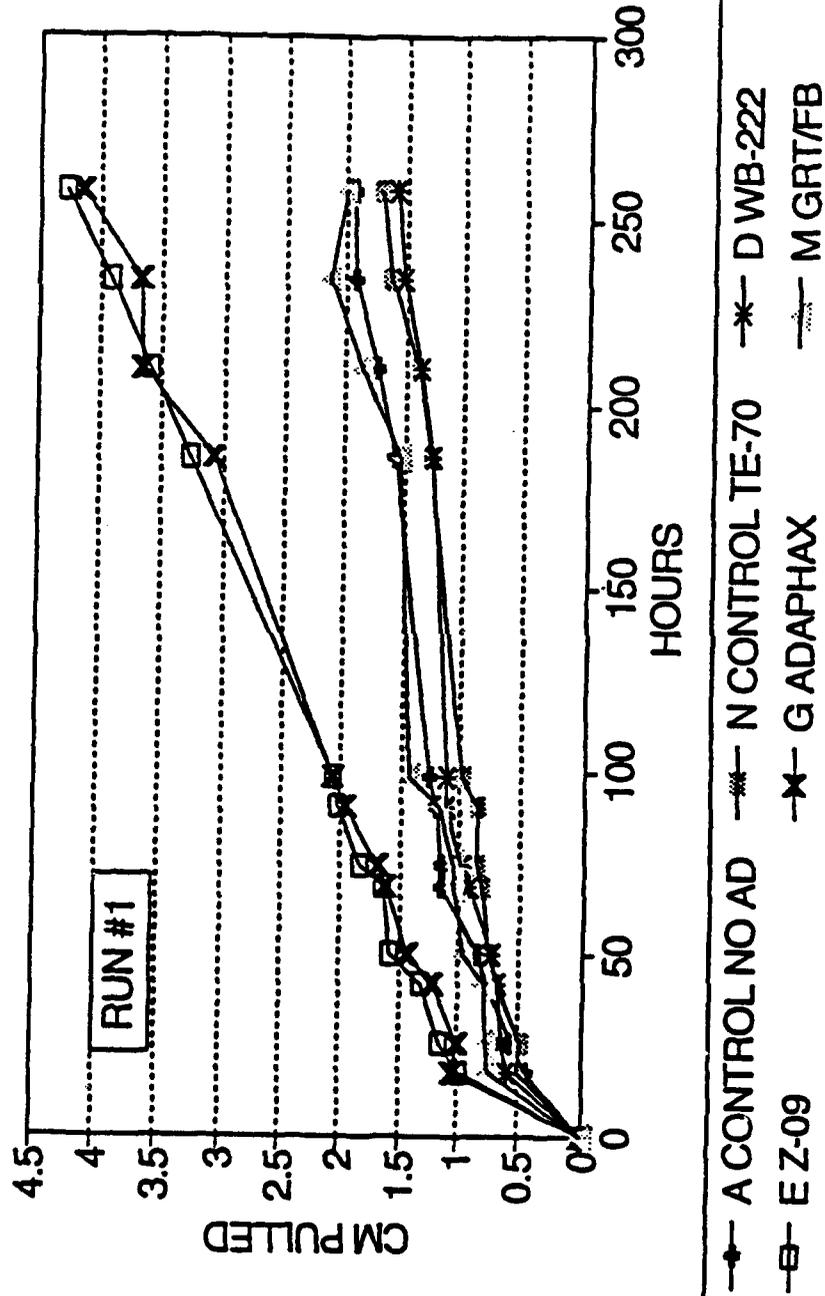


Fig. 1 - Adhesion Test, Run 1, Cathodic Delamination Test

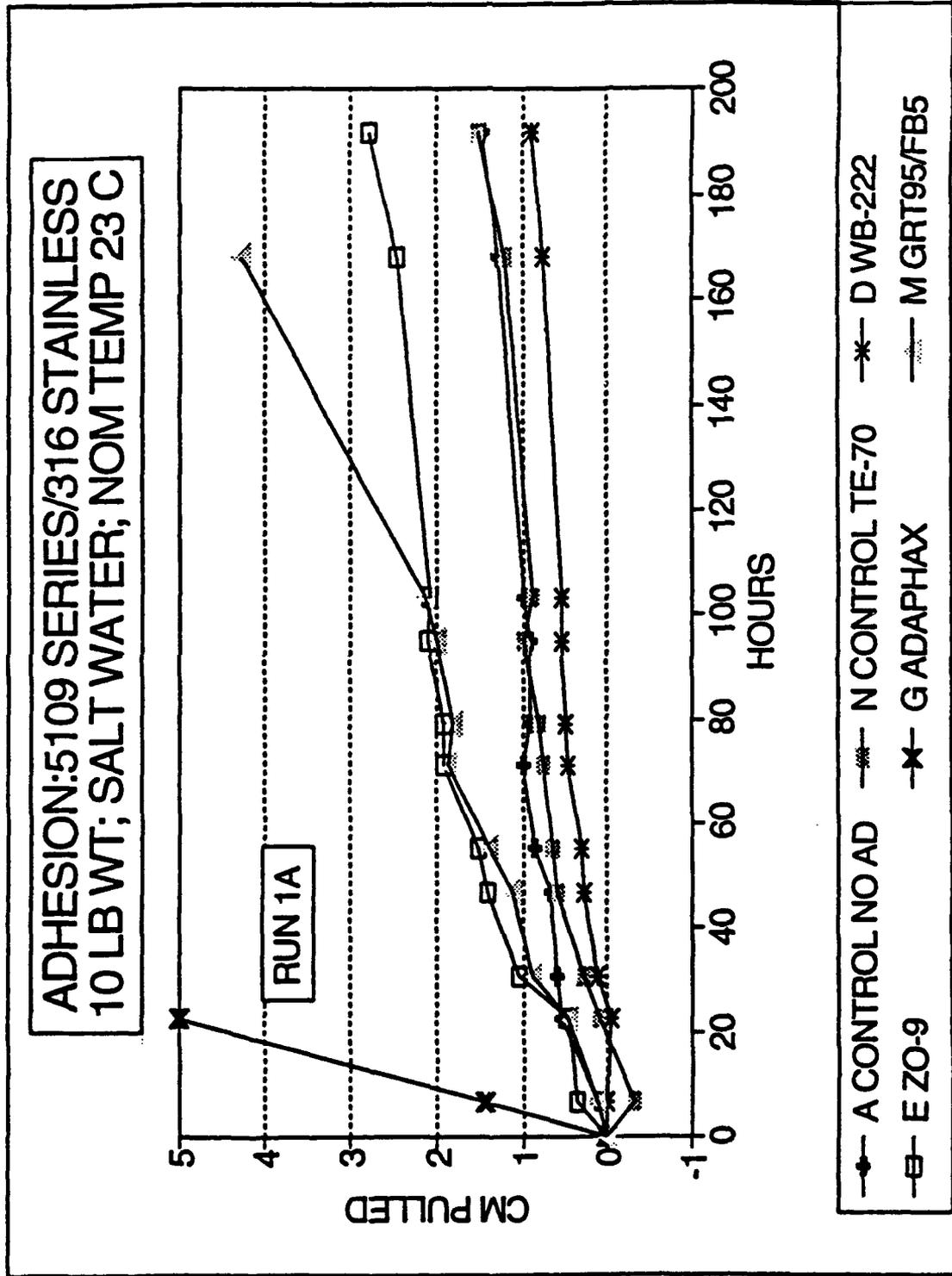


Fig. 2 - Adhesion Test, Run 1A, Cathodic Delamination Test

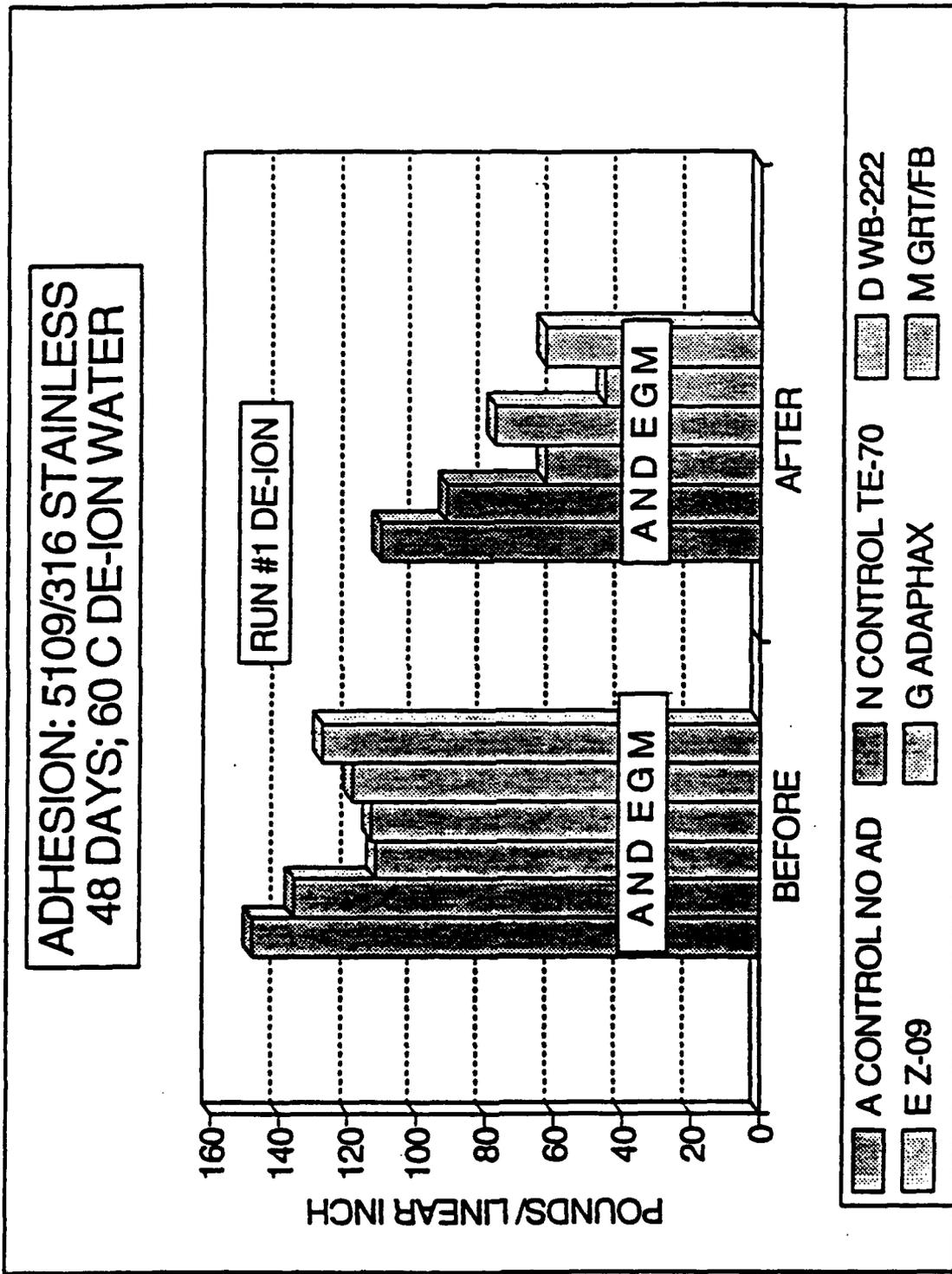


Fig. 3 - Adhesion Test, Run 1, Deionised Water Test

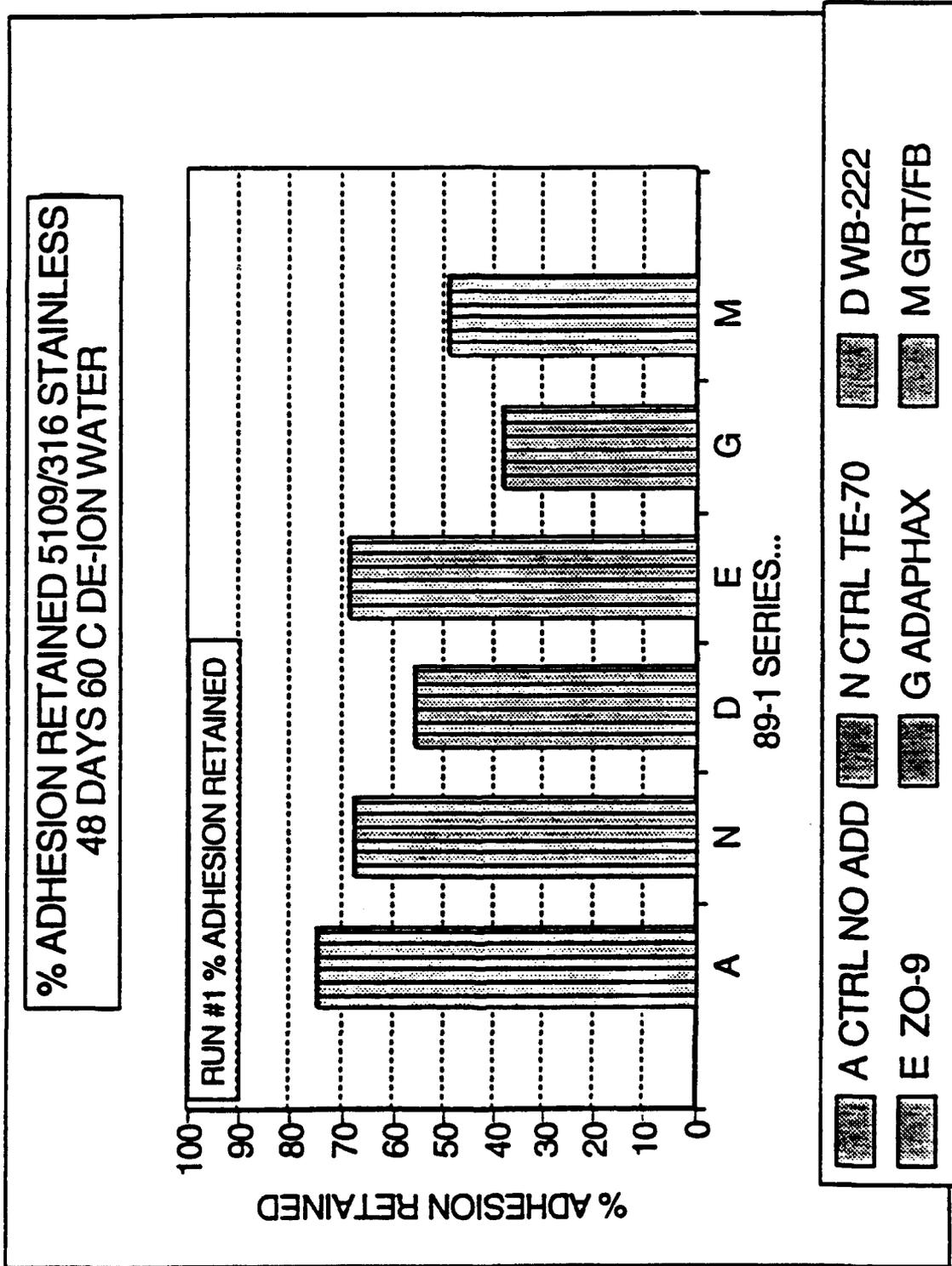


Fig. 4 - Adhesion Test, Run 1, % Adhesion Retained Test

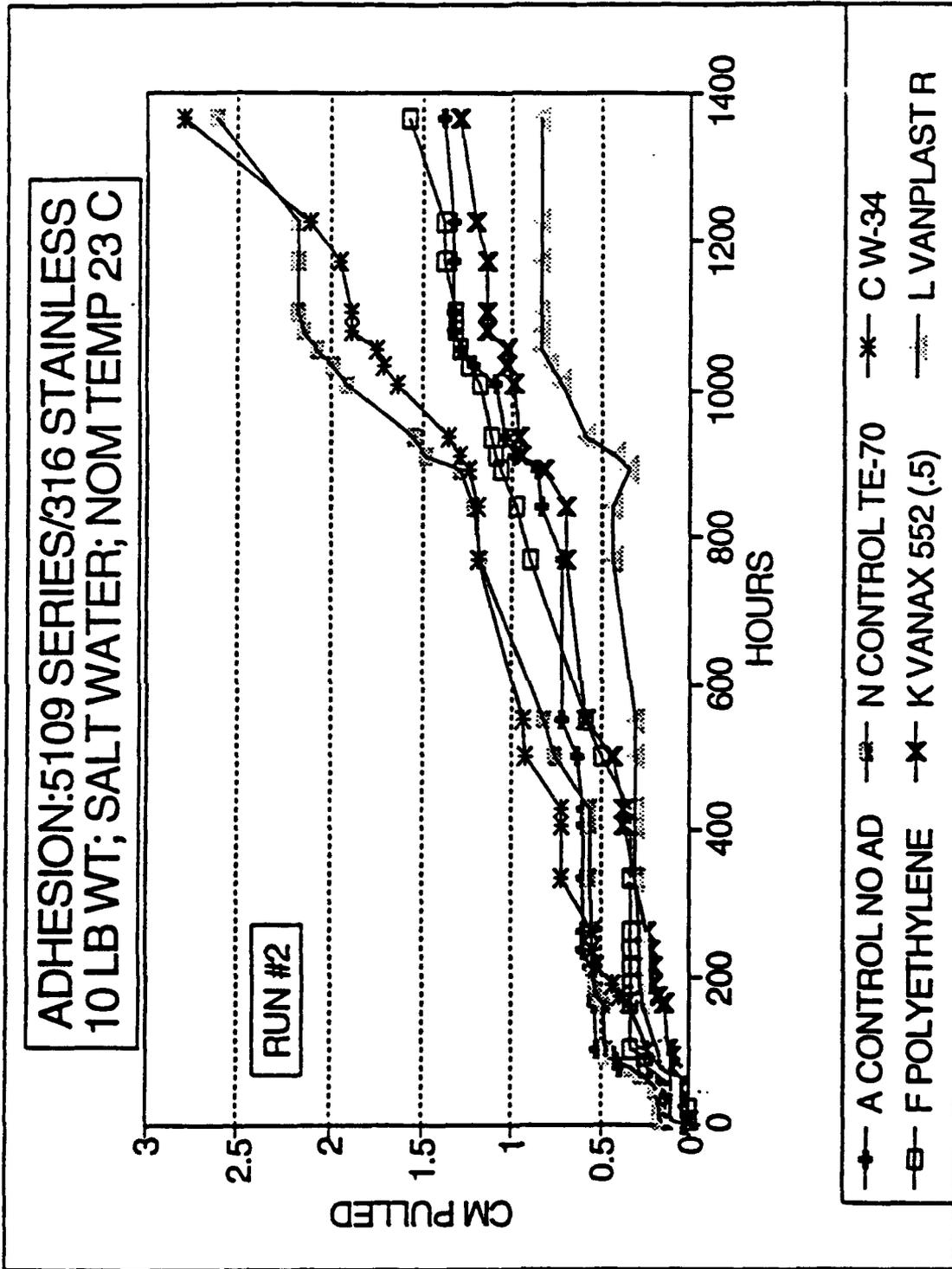


Fig. 5 - Adhesion Test, Run 2, Cathodic Delamination Test

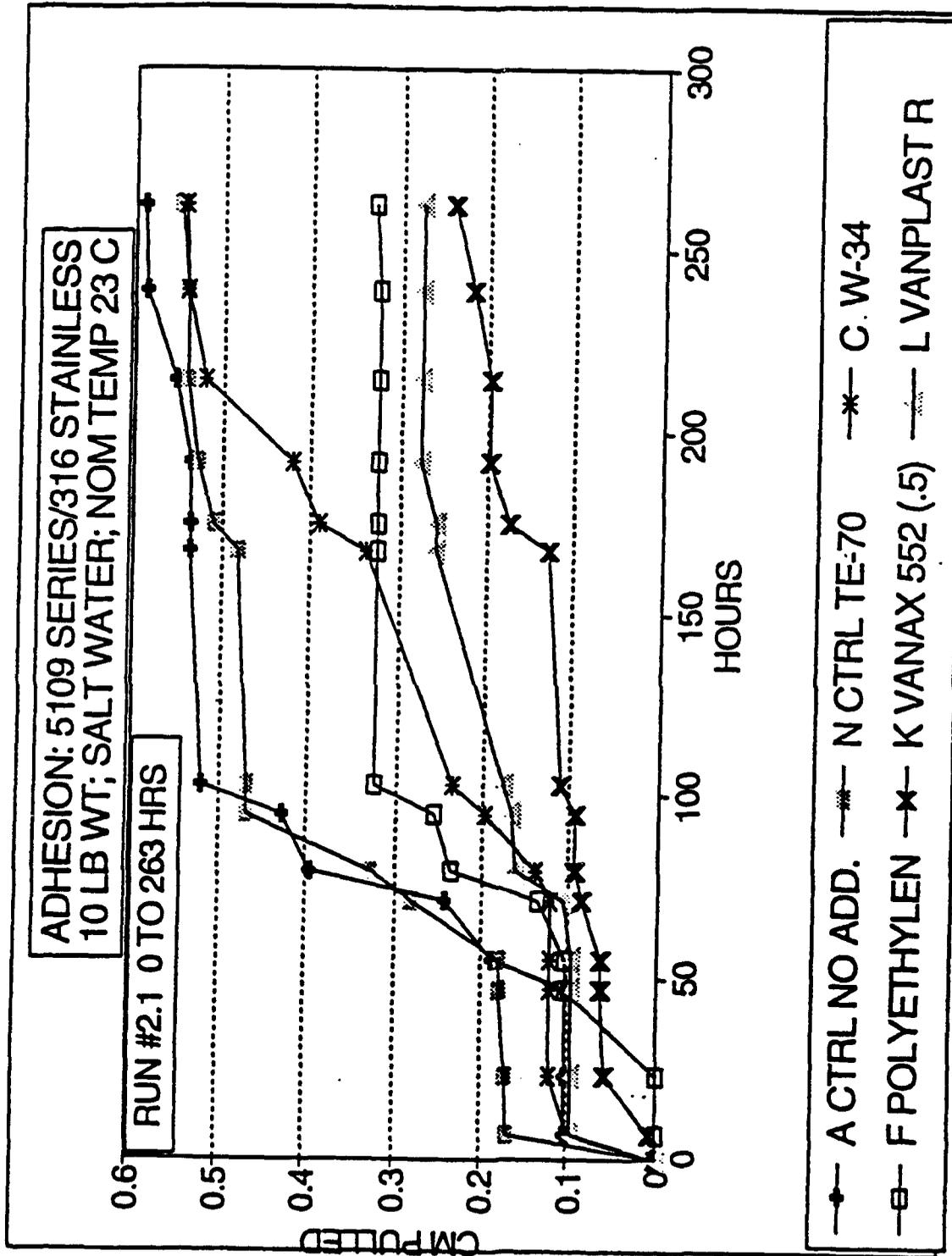


Fig. 6 - Adhesion Test, Run 2.1, Cathodic Delamination Test

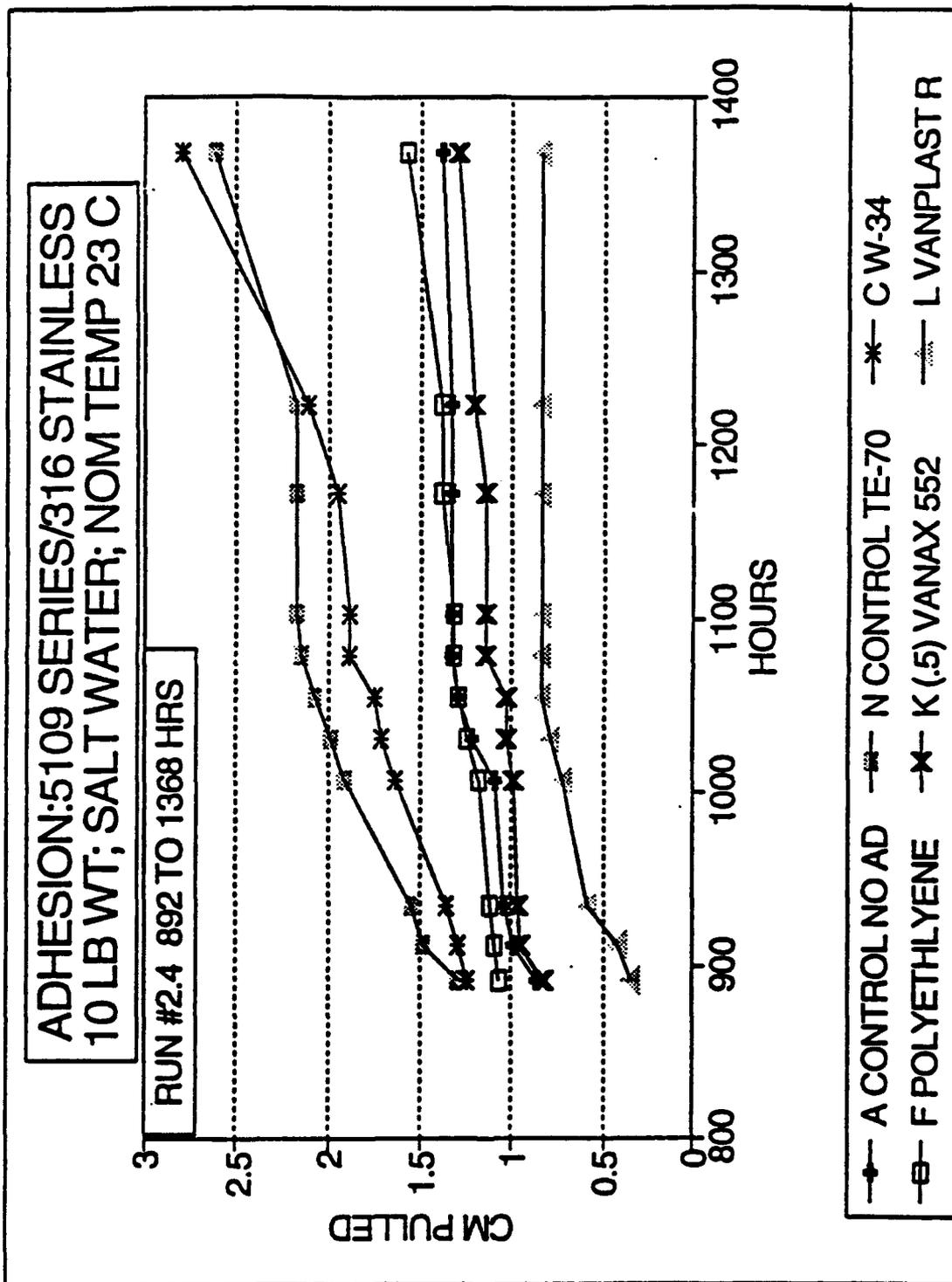


Fig. 7 - Adhesion Test, Run 2.4, Cathodic Delamination Test

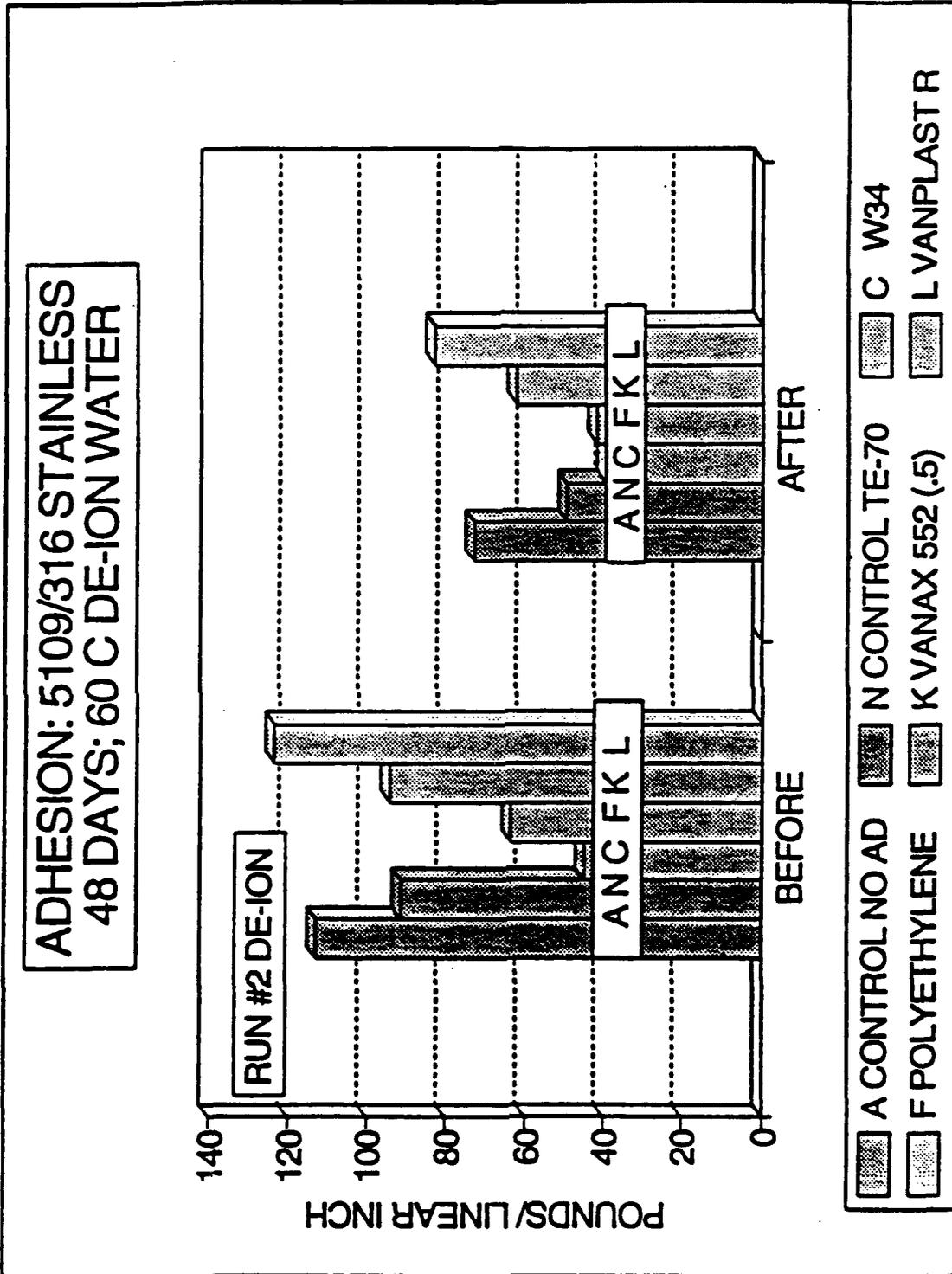


Fig. 8 - Adhesion Test, Run 2, Deionized Water Test

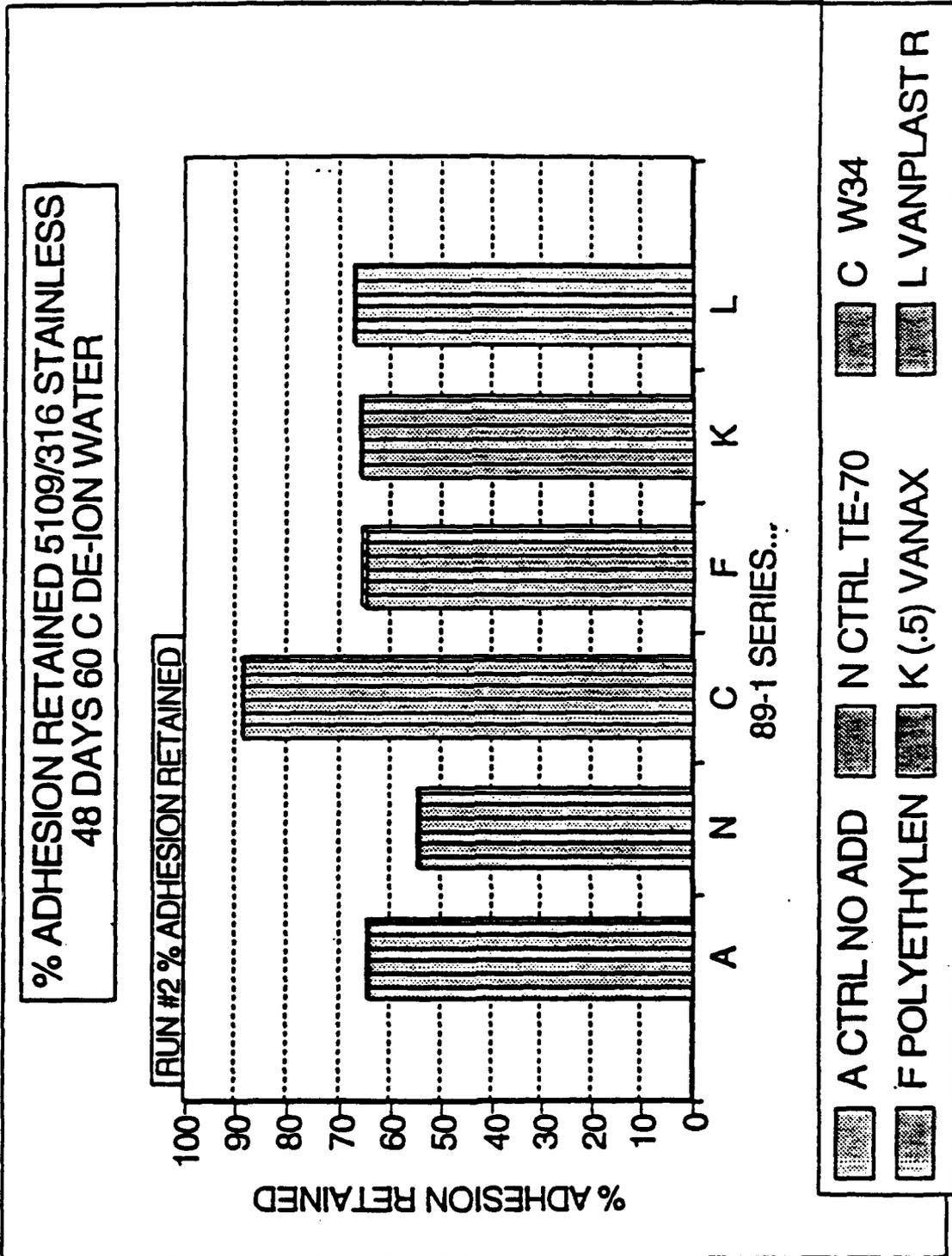


Fig. 9 - Adhesion Test, Run 2, % Adhesion Retained Test

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Appendix

MATERIALS LIST

Neoprene GRT	Du Pont, Vanderbilt
Stearic Acid	Hall, Harwick, Akrochem
Octylated diphenylamine	Vanderbilt, Hall, Harwick
MBTS	Vanderbilt, Harwick, Monsanto
Red Lead Dispersion	Ware, Kenrich, Disco
N-550 Carbon Black	Cabot, Columbian, Richardson
TE-70	Technical Processing Co.
W-34	Struktol Co.
WB-222	Struktol Co.
ZO-9	Disco Inc.
Polyethylene	Harwick
Adaphax 758	Vanderbilt
Cis 1,4 Polybutadiene	Polysar, Phillips
Vanax 552	Vanderbilt
Vanplast R	Vanderbilt
Neoprene FB	Du Pont, Vanderbilt
Chemlok 205	Lord Elastomer Products
Chemlok 220	Lord Elastomer Products