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NATIONAL BUREAU OF STANDARDS REPORT

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Progress Report

April 1 through June 30, 1969

DEVELOPMENT OF METHODS OF TEST FOR QUALITY CONTROL OF PORCELAIN ENAMELS

NBS

U.S. DEPARTMENT OF COMMERCE

NATIONAL BUREAU OF STANDARDS

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DEVELOPMENT OF METHODS OF TEST FOR QUALITY CONTROL OF PORCELAIN ENAMELS

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SUMMARY

Preliminary tests were made on porcelain enamel cover coats direct-to-steel to determine whether a double cantilever direct-pulling test could be adapted to measure the adherence of these porcelain enamels to their substrates.

Work was completed on the development of a Continuity of Coating test method for general purpose enamels.

A cupric chloride accelerated test method is described, which appears to give a more specific indication of color changes found for porcelain enamels on aluminum during three years of natural weathering, than does the boiling acid solubility.

The Double Cantilever Approach to the Adherence of Porcelain Enamel Cover Coats Direct-to-Steel

INTRODUCTION

Fracture mechanics is a relatively new discipline which relates the fracturing behavior of flawed bodies to applied loads. By its concepts, one defines a quantity, the fracture toughness, which has a similar importance in brittle failure that yield strength has in ductile failure. In a ductile material the load at which deviations from elasticity occur is associated with the yield point. In a cracked body the load that causes a stationary crack to propagate rapidly is associated with the fracture toughness. Hence the fracture toughness of a material is seen to be a measure of its ability to resist extension of a pre-existing crack. The parameter, fracture toughness, may be defined as the critical strain energy release rate

$$G_c = \frac{P^2}{2b} \left(\frac{d^{1/M}}{dc} \right) \quad . \; . \; . \; . \; . \; (1)$$

in units of pounds per inch.

where P is the load at which a crack propagates.
b is the specimen width
1/M is the reciprocal slope of the load-separation curve, and
c is the existing crack length before propagation.

The double cantilever method has previously been used to study many metals, tranclucent crystals, transparent glass, flawed concrete, brittle plastic materials and electrical porcelain. The appended bibliography refers to some of these applications. This investigation was initiated to explore whether the fracture toughness of porcelain enameled cover coats direct-to-steel can be used to evaluate the force required to strip an enamel coating from its substrate. A pre-existing crack will tend to advance through the weakest plane within the coating-substrate system. Thus the fracture toughness value will evaluate the adherence of the coating only if the separation occurs between the coating and substrate.

RESULTS AND DISCUSSION

The experimental set-up includes a tensile testing machine with appropriate hardware to apply load to a specimen assembly. A specimen assembly consists of a direct-on specimen between two alluminum alloy bars, one of which is epoxied to the slightly sandblasted enamel surface, and the other is attached with the same adhesive to the bottom surface of the steel substrate.

A linear variable differential transformer, L.V.D.T., is mounted to measure and record small changes in separation between the cantilevers. A typical geometry for the specimen assembly is shown in Figure 1.

It can be seen by referring to Figure 1 that in the initial situation the force P acts through moment arms c, (equal to the effective cantilever length) and strain energy builds up at the leading specimen edge. When the strain energy exceeds a critical value, a crack will propagate through the weakest path. As the crack increases in length so does the effective cantilever length. The increased deflection of the lengthened cantilevers results in a decreased load on the specimen assembly and crack propagation will be temporarily arrested if the rate of cross head movement is slow enough.

A. Estimation of the Crack Length, c.

For transparent materials measurements of each crack length can easily be made during the tests. For opaque materials, in which the crack lengths cannot be readily observed, previous investigators have used a relationship between the reciprocal slope of the load-separation curve and the crack length to establish the latter quantity.

Calibration bars of height 2h plus specimen thickness were prepared from the aluminum alloy material. Saw cuts of various lengths were used to simulate a range of crack lengths. The reciprocal slope of the load-separation curves of these calibration bars, shown in Figure 2, served to establish the relationships plotted in Figures 3 and 4. The crack length within specimen assembles employing similar alloy cantilevers can then be estimated from the 1/M of a load-separation curve using the relation shown in Figure 3.

The relationship between 1/M and c was obtained from the equation of the straight line of the straight line of the log-log plot.

$$\log 1/M = 1.4917 + 2.0487 \log c \quad \ldots\ldots (2)$$

$$\log c = \frac{\log 1/M - 1.4917}{2.0487} \quad \ldots\ldots (3)$$

The value of c was obtained directly from its logarithm. In addition a polymomial, in terms of crack length, c, was fitted to the experimentaly determined values of 1/M, the relationship between 1/M and c was assumed to be

$$1/M = A + Bc^2 + Cc^3 + Dc^4 \quad \ldots\ldots (4)$$

where A, B, C, and D are constants.
Thus

$$\frac{d(1/M)}{d\ c} = 2Bc + 3Cc^2 + 4Dc^3 \quad \ldots\ldots\ldots\ldots (5)$$

B. Calculations of Fracture Toughness, Gc

A specimen bank has been established which includes three groups of direct-to-steel cover coats, each of supposedly differnt adherence values. Three degrees of pickling were employed in the preparation of these specimens, varying from normal pickling, through an intermediate degree to an insufficient or zero amount.

Several trials of the double cantilever method outlined above, have been made. These were made primarily to develop the details of the experimental techniques and also to give preliminary evaluation to the same enamel on the same substrate after different degrees of pickling. Enamel B was selected to give a comparison between normal and, in this case, no pickling. The results calculated from Equation (1) are given in Table 1. Eight crack propagations are given for the normally pickled system leading to eight values of Gc with a mean value of 1.6 pounds per inch (of width). Lesser numbers of crack events were usable when the pickling was inadequate. Only those cracks were used for which the slope of the load-separation curve diminished from the previous value. It can be seen that the values of Gc for the unpickled specimens had a mean value of 0.03 pounds per inch, or less than two percent of the value for the normally pickled substrate systems.

C. The Mode of Failure Observed in the Trials

The unpickled specimens failed in such a way that the glass and oxide layers were cleanly separated from the bright metal substrate for the full width of the cantilevers (o.5 inch). The weakest adherence was between the oxide layer (black) and the bright substrate. The values of 0.03 pounds per inch were an evaluation of the adherence sought.

The coating of the normally pickled speciment was not stripped cleanly from the substrate. Approximately one half of the coating was removed exposing the black oxide layer but practically no bright metal. The fracture toughness, here evaluated, corresponded to the adherence of the glass layer to the oxide layer. One can assume this to be the interface of poorest adherence. The irregularity in glass removal may possibly be attributed to insufficient adhesive strength of the epoxy to the glass layer. Also this irregularity was undoubtedly reflected in the fairly large variability in the Gc values calculated for this enamel system.

<u>PLANS FOR NEXT REPORT PERIOD</u>

1. Evaluate the fracture toughness of several other enamel systems which differ only in pickling pretreatment.
2. Seek improved epoxy adhesives or better technique in their use.

3. A portable adherence measuring device manufactured by the Gardner Laboratory for use primarily with organic coatings is available. This is a self-contained force measuring device. It will be tried on cover coats direct-to-steel prepared after various pretreatments.

CONTINUITY OF COATING

During this report period, a second dc high-voltage apparatus was borrowed to determine whether two dc instruments would give more consistant results than the four ac instruments did. It was found that the air gap - voltage curves for the dc instruments were different but the "critical overvoltage" remained constant. Therefore, the original test precedure was modified so only the air-gap voltage needs to be determined for each test instrument. Once this is determined, the same electrical stress may be added to any enamel by adding a given overvoltage to the air gap voltage for the instrument being used. If ac instruments are used, the air-gap voltages and the overvoltage must be converted to peak voltages by multiplying by 1.414.

These changes were incorporated into the papers describing the development of this test and the test procedure. Both of these papers have cleared the editorial review at the National Bureau of Standards and have been submitted for publication to the American Ceramic Society and PEI.

WEATHERING OF PORCELAIN ENAMELS

The inspection of the enamels on aluminum included in the 1966 Exposure Test of Porcelain Enamels on Aluminum was completed during the quarter ending March 31, 1969. Upon completion of this inspection, it was noted that the boiling acid solubility test did not correlate well with the color retention of many of the enamels exposed at Kure Beach. Therefore some time was devoted toward the development of a new test that might correlate better with actual results than the boiling acid solubility test. The test developed utilized the same apparatus as the boiling acid solubility test exceptthat 50 ml of a 12.5 percent solution of cupric chloride is substituted for 150 ml of 6 percent citric acid. The cupric chloride is boiled on the specimen surface for one hour, poured out, and the specimen surface is rinsed with 10 ml of a one percent solution of oxalic acid to remove any green copper stains that may have formed. The specimens are then removed from the clamping devise, washed with a mild detergent solution, rinsed with tap water, distilled water and alcohol and allowed to dry in a near vertical position. When the specimens are dry, the color change between the tested and untested portions of the specimen is measured and is used as a measure of the enamel's weather resistance. This test produces color changes in the enamels which are similar to those occurring during natural weathering. Figures 6 and 7 compare the color retentions at Kure Beach and Los Angeles vs boiling acid and cupric chloride test results. A better correlation exists between the cupric chloride specimens and color retention than between the boiling acid solubility treated specimens and color retention. It is felt that the cupric chloride test may be a better test for predicting the weatherability of these enamels but it is also felt that exposure data for longer periods of time are needed to determine whether these same color changes will occur at the milder sites. If the large color changes are confined to Kure Beach, then more work will have to be done to determine the cause of the severity at this site.

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Table 1. Values Obtained for the Fracture Toughness, G_c for a Porcelain Enamel Cover Coat Direct- to-Steel.

Direct-On Enamel	Crack No.	Slope of Load-Deflection Curve	Crack Length	Load to Propagate Crack		Fracture Toughness, G_c
		Pounds/microinch	In.	Pounds		Pounds/inch
		$\times 10^3$				
B	2	6.08	2.26	86.9		1.07
(Normal	3	5.01	2.48	82.7		1.15
Pickle)	4	2.75	3.32	79.0		2.05
	5	1.59	4.34	45.1		1.46
	6	1.19	4.99	37.8		1.61
	7	0.98	5.49	33.7		1.73
	8	0.81	6.02	29.0		1.75
	9	0.65	6.71	26.3		2.06
					mean	1.61
B	4	1.42	4.58	6.13		0.0320
(Not Pickled)	5	1.17	5.03	4.85		.0271
	6	0.98	5.49	4.13		.0261
	8	0.78	6.13	3.34		.0246
	9	0.69	6.50	2.86		0.0219
					mean	0.0263
B	2	3.83	2.83	11.8		0.0309
(Not Pickled)	3	2.66	3.38	9.37		.0303
	4	1.12	5.13	4.93		.0299
					mean	0.0304

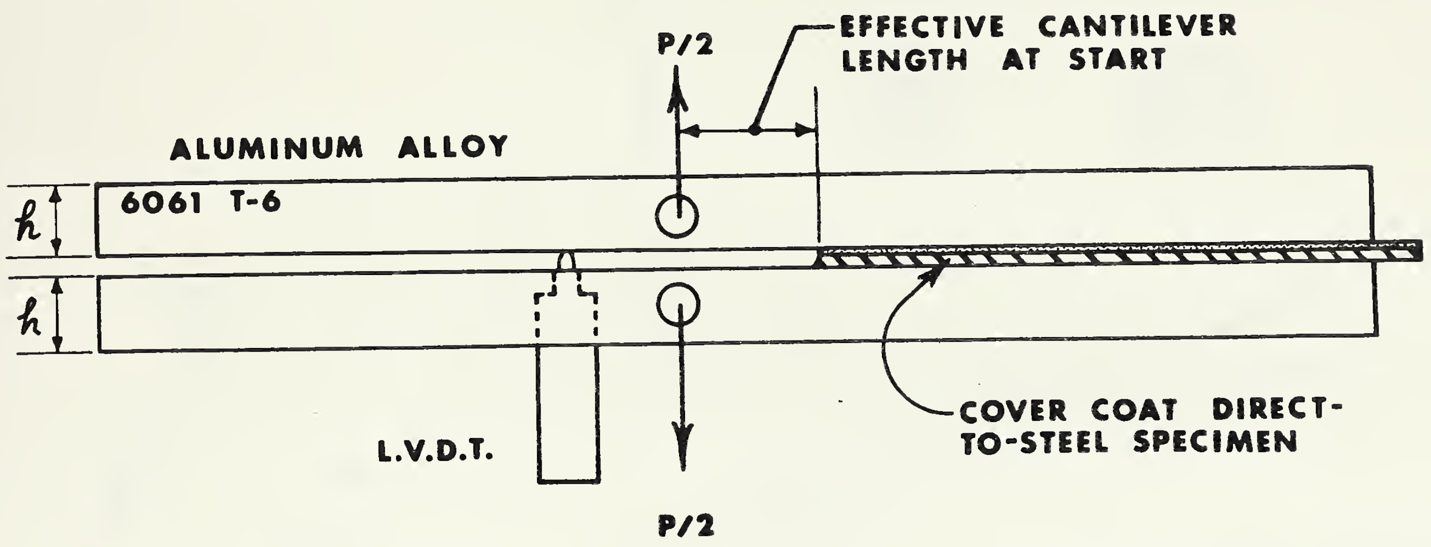

FIGURE 1.

DOUBLE CANTILEVER SPECIMEN ASSEMBLY

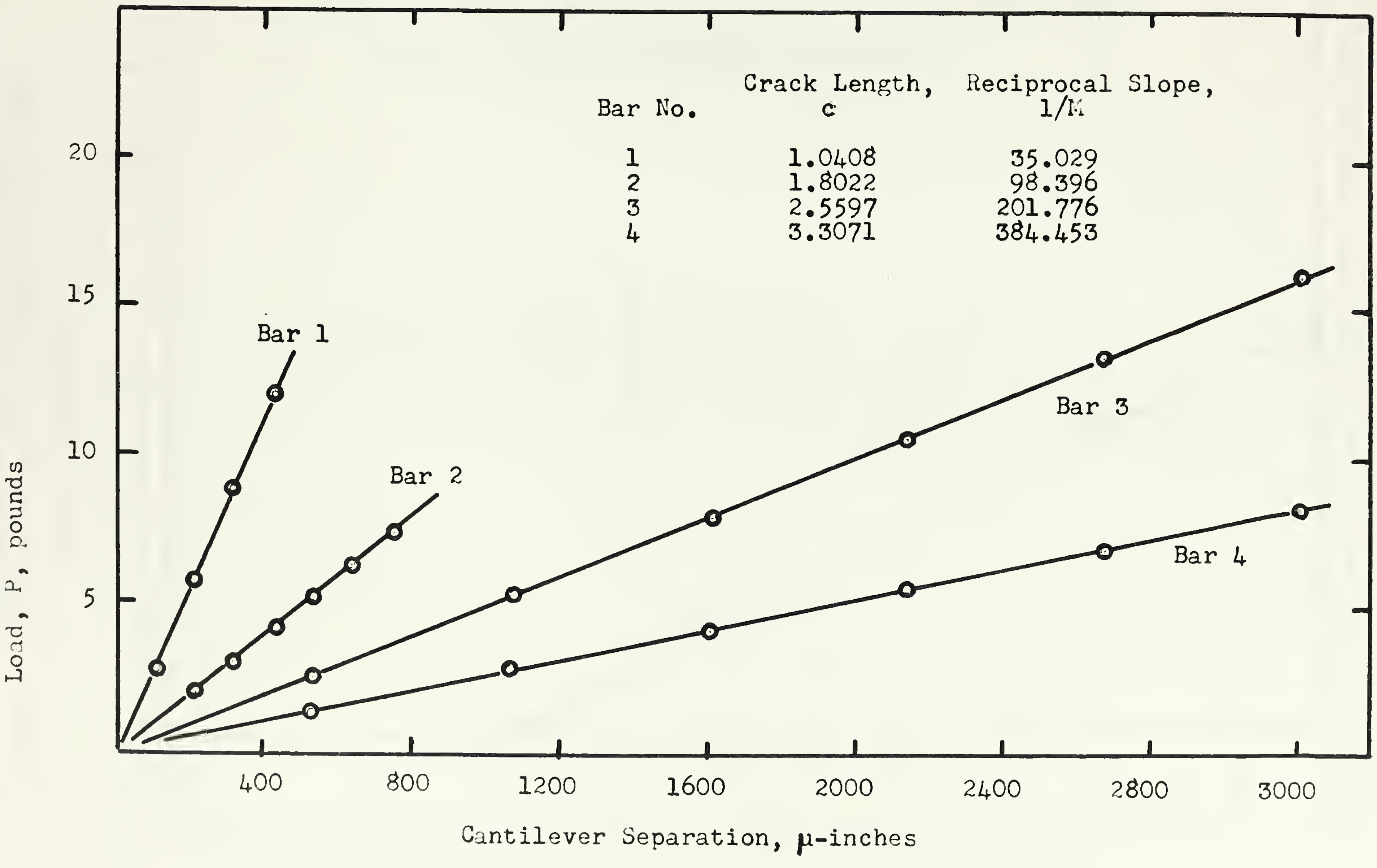

Figure 2. Load-Separation Curves for Calibration Bars

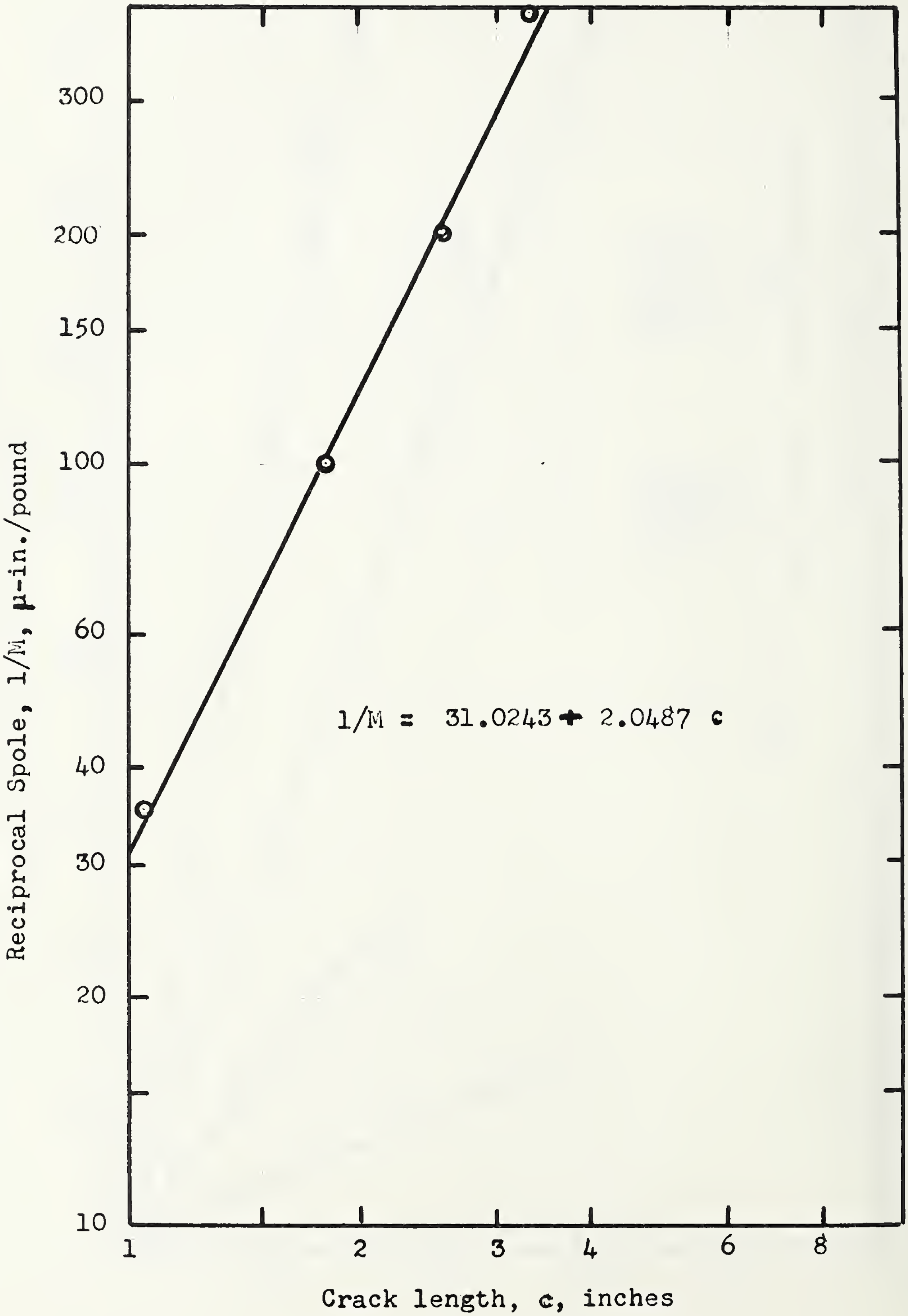

Figure 3. Log-Log Plot of Reciprocal Slope, 1/M and Crack Length for Calibration Bars.

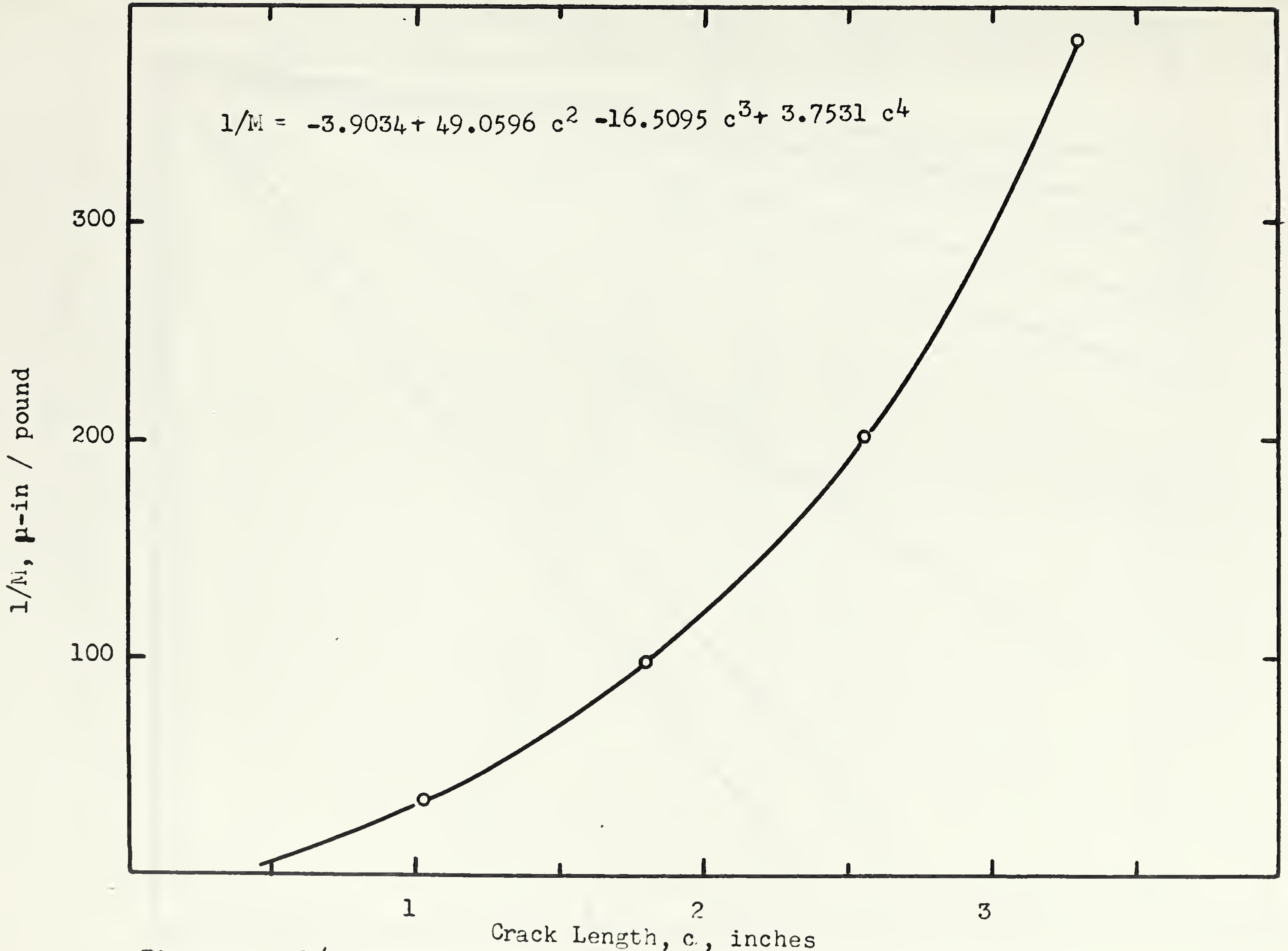

Figure 4. 1/M for Calibration Bars With Different Crack Lengths.

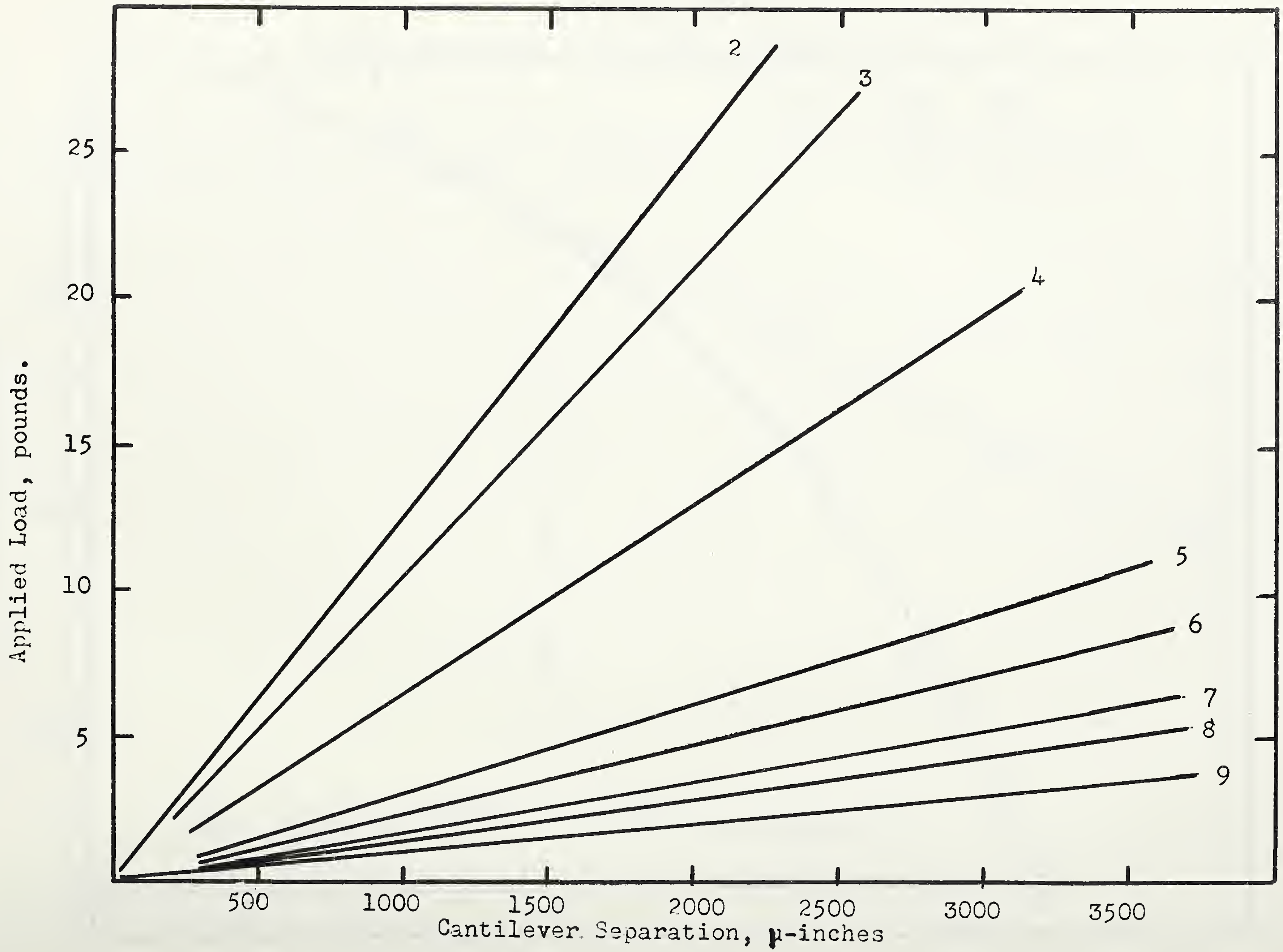

Figure 5. Superimposed Load-Separation Curves for Cracks 2 thru 9 of a Specimen.

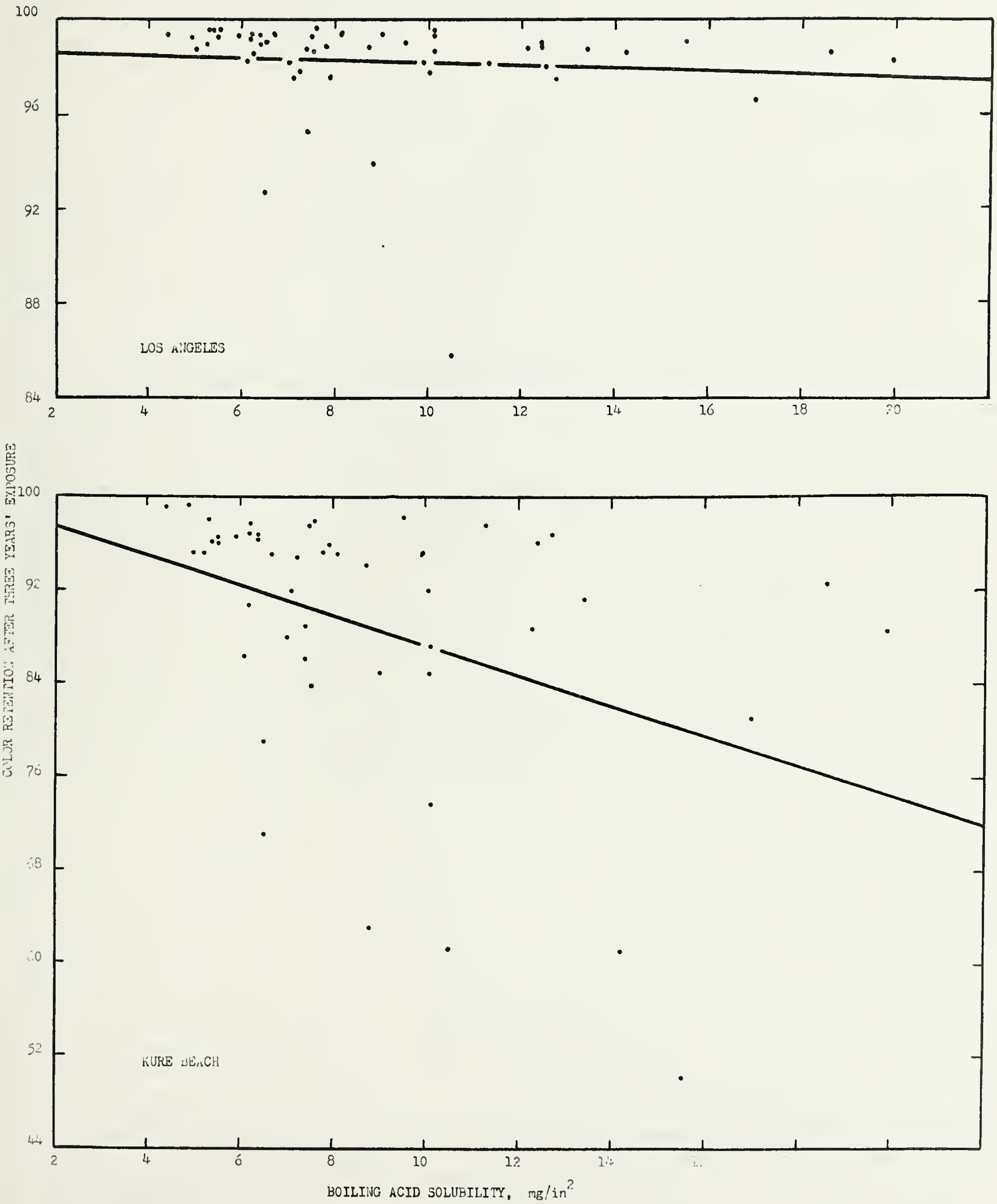

Figure 6. Correlation between the Boiling Acid Solubility Test and Color Retention of Enamels Exposed Three Years at Los Angeles and Kure Beach.

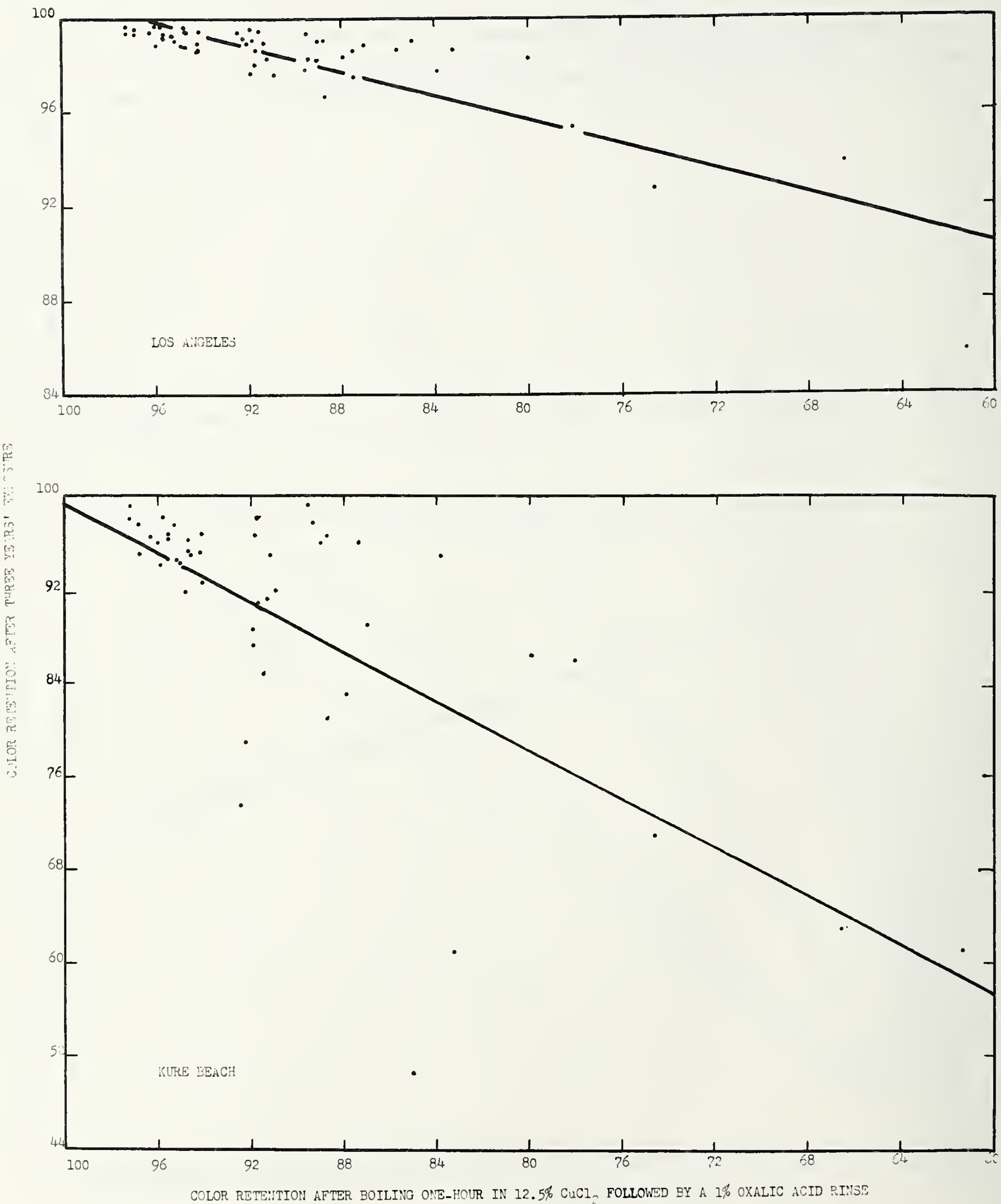

Figure 7. Correlation between the Cupric Chloride Treatment and the Color Retention of Enamels Exposed Three Years at Los Angeles and Kure Beach.

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