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Defect Area Determination of Organic Coated Steels in Seawater Using the Breakpoint Frequency Method

by
Harvey P. Hack
John R. Scully

DTRC-SME-89/45 Defect Area Determination of Organic Coated Steels in Seawater
Using the Breakpoint Frequency Method.



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with and without an intentional defect. A correlation was obtained between the breakpoint frequency and visually estimated electrochemically active area on epoxy coatings of a variety of thicknesses. This method offers a simple alternative to determination of defect areas via the use of the pseudocapacitance from difficult-to-analyze low frequency impedance data. This approach also can detect the beginnings of coating breakdown long before visual indications are present.

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ABSTRACT

Coating breakdown is a major maintenance cost on ships. It is therefore desirable to have a rapid technique for predicting or evaluating coating performance non-destructively. A method for simply determining the extent of coating breakdown would therefore be of great use to the Navy.

The breakpoint frequency method is described which allows determination of the electrochemically active area of a coated metal in seawater. A computer model is used to explain the basis of the breakpoint method, and the model is compared to impedance and visual data from epoxy coated steel panels in ASTM artificial seawater with and without an intentional defect of known area.

The breakpoint frequency method was found to be extremely useful in determining the electrochemically active area of coated steel in seawater. The equivalent circuit model used in this analysis was found capable of fitting actual data on coated steel panels with and without an intentional defect. A correlation was obtained between the breakpoint frequency and visually estimated electrochemically active area on epoxy coatings of a variety of thicknesses. This method offers a simple alternative to determination of defect areas via the use of the pseudocapacitance from difficult-to-analyze low frequency impedance data. This approach also can detect the beginnings of coating breakdown long before visual indications are present.

ADMINISTRATIVE INFORMATION

This project was supported by the DTRC Ship and Submarine Materials Block Program under the administration of DTRC Code 0115. The program coordinator is Mr. Ivan Caplan. The work described was performed under Work Unit 1-2813-959 and satisfies milestone CT6/4. The work was conducted at DTRC in the Marine Corrosion Branch, Code 2813, under the direction of Mr. Robert Ferrara.

INTRODUCTION

Coating breakdown is a major maintenance cost on ships. It is therefore desirable to have a rapid technique for predicting or evaluating coating performance non-destructively. A method for simply determining the extent of coating breakdown would therefore be of great use to the Navy.

A good organic coating will protect the steel beneath it except at blisters and holidays, and only at these defects will corrosion occur. Similarly, the high resistance of a good coating will cause the principal cathodic protection current demand to be determined from the defect areas. The area of coating defects is therefore important to know in order to determine corrosion rate from polarization data and to determine cathodic protection requirements. The percentage of defect area is also a good indication of coating quality and need for coating repair.

One possible method for determining the electrochemically active area under coating defects is by the use of interfacial capacitance measurements. This requires knowledge of specific capacitance (per unit area). In traditional aqueous electrochemistry, the double layer capacitance per unit area is usually considered similar to that for mercury, 15 to 30 $\mu\text{F}/\text{cm}^2$.^[1,2] For corroding steel systems, "apparent" double layer capacitances are either found to be quite large (i.e. greater than 100 $\mu\text{F}/\text{cm}^2$), difficult to calculate, or both.^[3-6] For some corroding systems, sophisticated electrical equivalent circuit models have been used to determine the true interfacial capacitance, as it cannot readily be determined from raw impedance data.^[7,8] In other

cases, an adsorption psuedo-capacitance model has led to determination of a capacitance which is larger than $30 \mu\text{F}/\text{cm}^2$.^[6] The electrochemically active area is determined from the following expression:

$$\text{Area} = C_{\text{meas}}/C_{\text{specific}}$$

where C_{meas} is the measured capacitance, in μF , using either of the appropriate methods discussed above, and C_{specific} is the area specific capacitance in $\mu\text{F}/\text{cm}^2$.

Using the above approach requires the selection of the proper specific capacitance, which is not always straightforward. Additional complexity is introduced for organic-coated steels because of the heterogeneity of the development of the electrochemical processes at the metal interface. Both perpendicular and tangential resistive paths in the coating have to be considered in electrical equivalent circuit modeling in addition to the interfacial processes.^[9-12]

The purpose of this work was to evaluate a new approach to determining coating defect area which does not depend on rigorous analysis of lower frequency impedance data, as would be the case if coating resistance were to be determined. This approach, based on a technique discussed by Haruyama, et al. called the breakpoint method, uses high frequency data to obtain the electrochemically active area.^[13] The breakpoint frequency method has been found to be more accurate than the specific capacitance method in soil corrosion work.^[14] The correlation of the breakpoint frequency describing these

coating properties with defect area as determined by ASTM visual methods will be discussed.

THE BREAKPOINT FREQUENCY METHOD

One simple method used to model a good quality organic coating over steel in which a holiday exists is to use a nested, simplified Randles circuit as in Fig. 1. The bulk of the surface is covered with a coating with such high resistance as to be considered a pure capacitor, of value C_c . The defect consists of a region extending completely through the coating thickness, d , that has a resistivity sufficiently lower than the

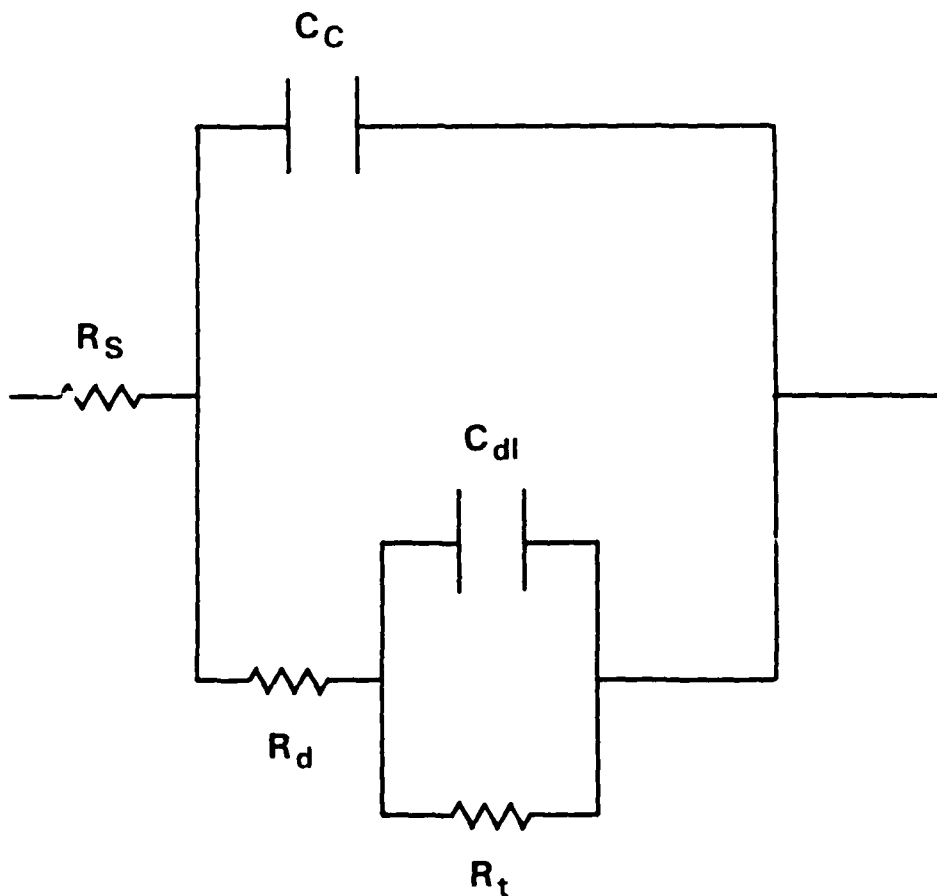


Fig. 1. Nested simplified randles circuit of a coated steel panel with a defect.

bulk coating to make electrochemical processes possible under that region. A defect could consist of a weak area of coating, or a crack or hole extending through the coating. This defect can be represented by its resistance through the coating thickness to the steel surface, R_d , in series with the parallel combination of a double layer capacitance (or interfacial pseudocapacitance), C_{dl} , and charge transfer resistance, R_t , associated with corrosion of the steel surface. The net impedance associated with the defect would be a function of defect area. In the modeling described below, R_d is assumed to have a resistivity similar to that of seawater, as though it were a hole filled with seawater, and R_t is assumed to be the same as for bare steel. Both of these assumptions are borne out to some extent by data shown below.

Varying the defect area percentage used with this equivalent circuit will lead to a family of curves, as shown in Figs. 2 and 3. These curves are for a total cell area of 10 cm² and defect area percentages as indicated. ASTM visual ratings for these same defect areas are also shown on the figures.

Breakpoint frequencies are shown on the Bode-Magnitude plot in Fig. 2 as the points where, descending the curve from higher to lower frequencies, a transition occurs from a capacitive region of slope = -1 to a resistive region of slope = 0. These same breakpoint frequencies are shown on a Bode-Phase plot in Fig. 3 as the points where, descending the curve from higher to lower frequencies, the phase shift first reaches 45 degrees.

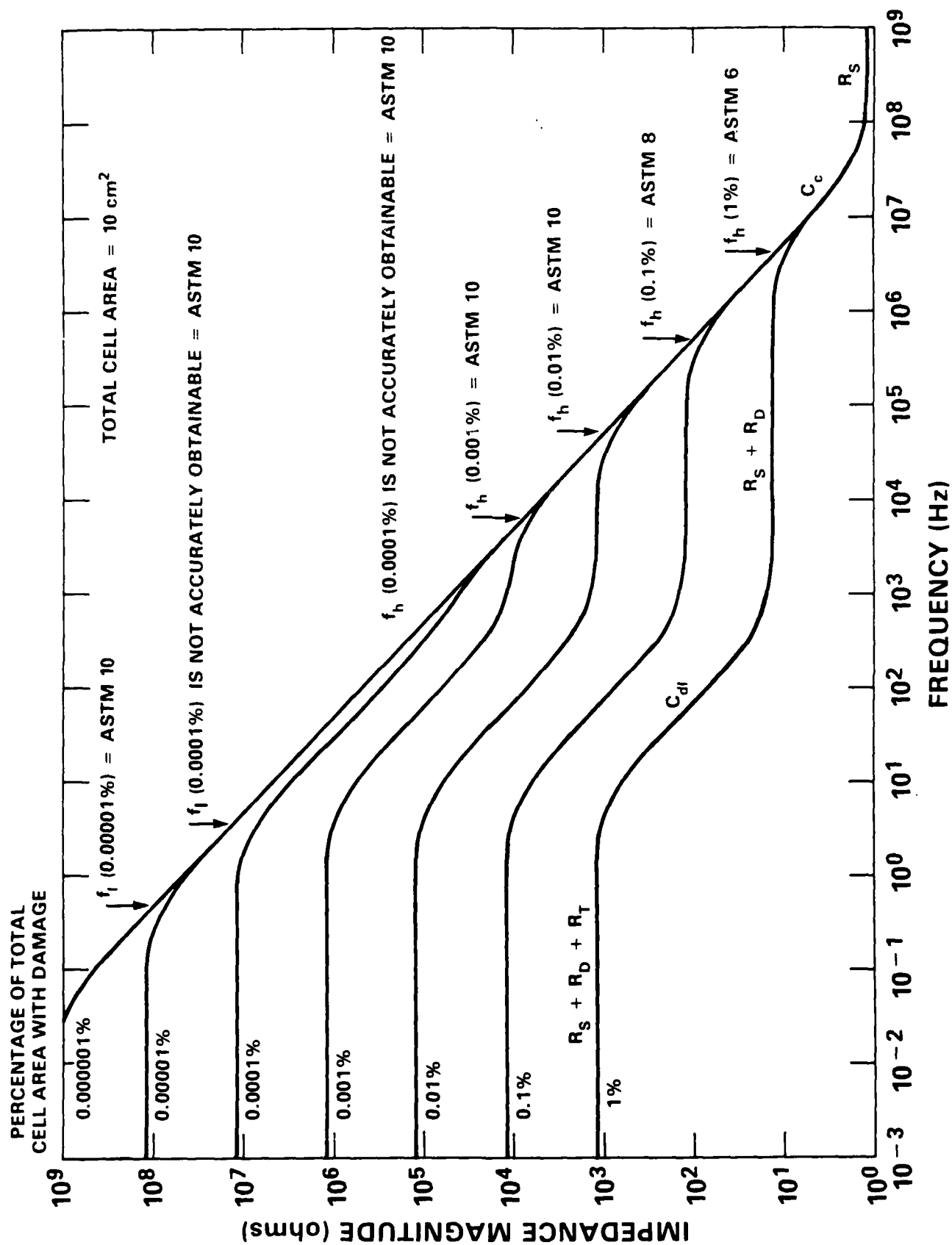


Fig. 2. Effect of defect area percentage on impedance magnitude behavior of a coated steel equivalent circuit. Total cell area assumed is 10 cm².

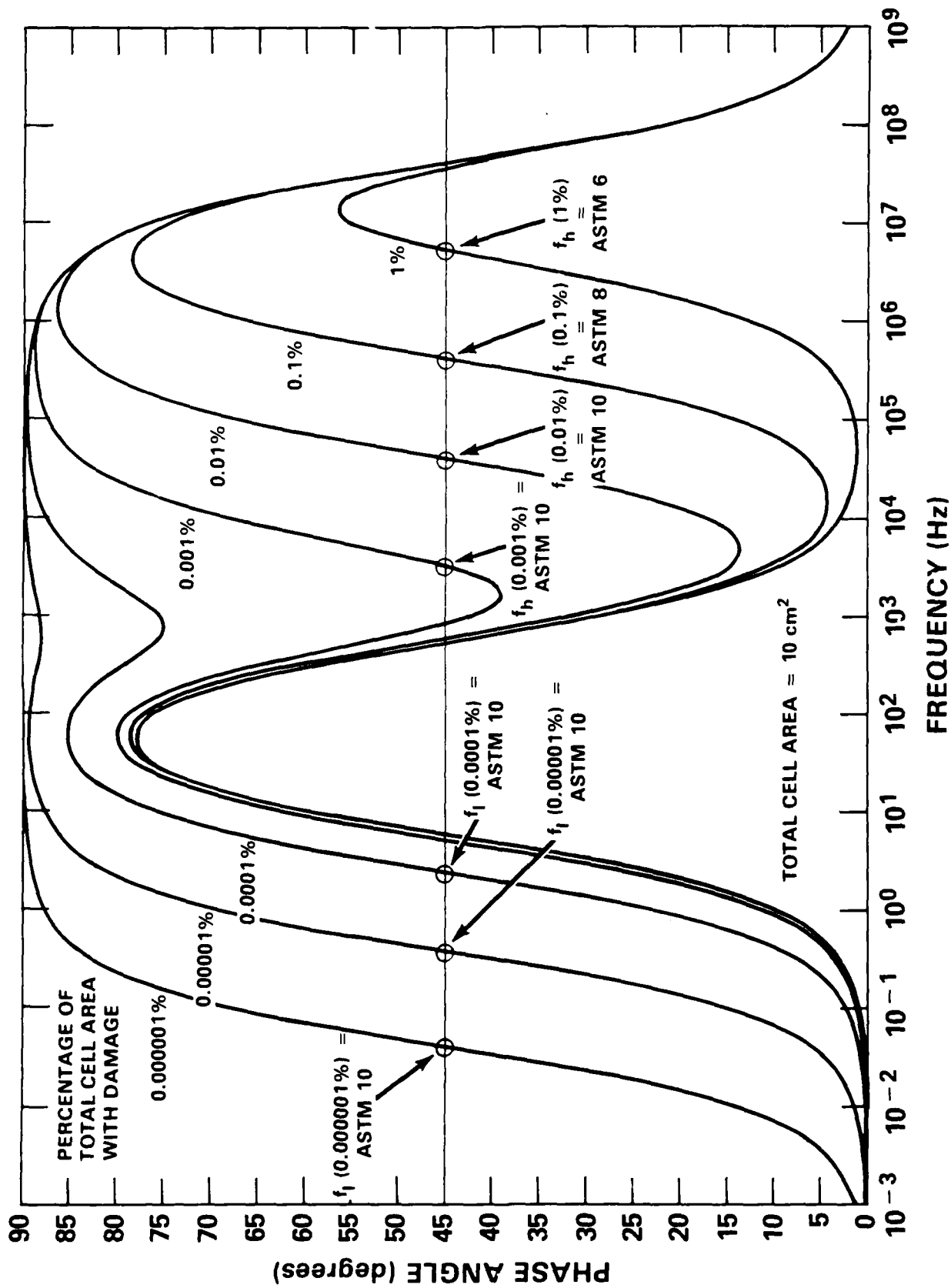


Fig. 3. Effect of defect area percentage on impedance phase behavior of a coated steel equivalent circuit. Total cell area assumed is 10 cm².

For larger defect area percentages, the point at which the coating impedance, $1/\omega C_c$, equals the defect resistance, R_d (plus the solution resistance, R_s , which is frequently negligible by comparison), is called the higher breakpoint frequency. This frequency, designated f_h following the notation of Haruyama, et al,^[13] will be a direct function of the defect area percentage. The relationship between this breakpoint frequency and defect area is derived as follows:

$$R_d = 1/(2 \pi f_h C_c) \quad R_d = \rho d/A_d \quad C_c = \epsilon \epsilon_0 (A-A_d)/d$$

where: A_d = defect area

A = fixed total specimen area

ρ = intrinsic coating resistivity at defect

d = coating thickness

ϵ = dielectric constant for the water-laden coating

ϵ_0 = permittivity of free space.

For defect areas of less than 1% of the sample area, $A-A_d$ is roughly equal to A and thus:

$$f_h = K A_d/A$$

where:

$$K = 1/(2 \pi \epsilon \epsilon_0 \rho)$$

A second, lower breakpoint frequency, designated f_l again following the notation of Haruyama, et al,^[13] will occur where the double layer impedance, $1/\omega C_{dl}$, equals the charge transfer resistance, R_t , plus the defect resistance, R_d (plus the solution resistance, R_s , again negligible by comparison). This frequency can be derived as follows:

$$R_t + R_d = 1/(2 \pi f_l C_{dl}) \quad R_d = \rho d/A_d \quad R_t = r_t/A_d \quad C_{dl} = A_d C_{dl}$$

where: r_t = unit area charge transfer resistance

C_{dl} = double-layer or pseudo- capacitance

c_{dl} = area specific double-layer or pseudo- capacitance

Thus: $f_1 = 1/(2 \pi c_{dl} (\rho d + r_t))$

For practical coatings in seawater, ρ of the defect is on the order of 1-10 ohm-cm (bulk resistivity of good coatings is on the order of 10^{12} ohm-cm), r_t is on the order of 10^3 ohm-cm², and d is on the order of 10^{-2} cm. This makes ρd roughly 4-5 orders of magnitude less than r_t and it can therefore be ignored. The equation then reduces to:

$$f_1 = 1/(2 \pi c_{dl} r_t)$$

This lower frequency is not dependent on defect area or cell area, but only on the relative magnitudes of the area specific double layer capacitance and charge transfer resistance of the defect.

Very small defect area percentages will lead to a situation where the defect resistance and double layer capacitance are not visible on the Bode-format figures due to poor separation of time constants. The higher breakpoint frequency, f_h , becomes unmeasurable, and the lower frequency, f_1 , becomes the frequency where the coating impedance, $1/\omega C_c$, equals the charge transfer resistance, R_t , plus the defect resistance, R_d (plus the solution resistance, R_s , still negligible by comparison). This frequency is a direct function of defect area:

$$R_t + R_d = 1/(2 \pi f_1 C_c) \quad R_d = \rho d / A_d \quad R_t = r_t / A_d \quad C_c = \epsilon \epsilon_0 (A - A_d) / d$$

Again assuming $A_d < 1\%$:

$$f_1 = K' A_d/A$$

where: $K' = d/[2 \pi \epsilon \epsilon_0 (\rho d + r_t)]$

Again assuming that ρd is much less than r_t , the equation then reduces to:

$$f_1 = K' A_d/A$$

where: $K' = d/(2 \pi \epsilon \epsilon_0 r_t)$

This area dependence of the lower breakpoint frequency will only be seen when the coating is very good, such that the total double layer capacitance, C_{d1} , is less than the total coating capacitance, C_c . This will occur when:

$$C_{d1} < C_c \quad \text{where: } C_{d1} = A_d C_{d1} \quad C_c = \epsilon \epsilon_0 (A - A_d)/d$$

or for $A_d < 1\%$: $A_d/A < \epsilon \epsilon_0 / C_{d1} d$

While f_h will always depend on defect area, the above analysis shows that f_1 is only dependent on defect area for very small defects where f_h is not resolvable (Figs. 2 and 3). This is also the only condition under which a breakpoint frequency is dependent on coating thickness.

Assuming that ρ , ϵ , and r_t remain relatively constant, or that changes in ϵ are compensated for by changes in ρ or r_t to keep K or K' constant, the breakpoint frequencies can be monitored over time. This is probably realistic for the coatings tested herein after 30 days exposure. As the coating degrades with time, the defect area should grow and the breakpoint frequencies get larger. At early exposure times

when there are few or small defects, f_i will be measured, but as the coating degrades, f_h will be the parameter determined during a scan from high frequencies to low frequencies.

The advantage of this method lies in its ability to obtain defect areas using the higher frequency part of the impedance spectra, without analyzing the complex behavior occurring at lower frequencies. In addition, a specific "bare metal" capacitance need not be used, with its associated uncertainties. The disadvantage is that during a measurement, it may not be immediately clear whether f_i or f_h is being measured. In practice, this is not a great disadvantage. Based on the model studies to date, the minimum value for a measurable f_h is about 100 Hz whereas the maximum value for f_i is about 10 Hz for the coatings and areas in this study. In practical systems, it is therefore usually possible to know which f is being measured simply by its value. An additional reason why this is not a problem is discussed below.

EXPERIMENTAL APPROACH

Cold rolled SAE 1010 1/4 hard steel panels (5 by 7 inches) with a 15-25 micro-inch ground surface were de-greased with xylene and coated with either opaque or transparent epoxy polyamides by a dip application method as in ASTM Standard D-823.^[15] The coatings were then allowed to cure fully. The opaque coatings were nominally defect free but may have contained microscopic latent discontinuities. Details for each coating type have been given elsewhere.^[10] Panels were exposed under freely corroding conditions in ASTM artificial ocean water at room temperature

with aeration provided by air bubbling (6 ppm dissolved oxygen concentration).

In one panel, an intentional defect of known area, 0.0066 cm², was created by drilling a small hole through a 70 µm transparent coating without penetrating the steel panel. Impedance data were collected on this panel with a cell placed over the defect after 3 hours exposure, and again with the cell over a different, undamaged area on the same panel after 24 hours exposure. At the time of the impedance measurement, the panel was momentarily removed from the seawater tank, and a cylindrical Lucite cell of 6.29 cm² area containing ASTM artificial ocean water was positioned on the panel surface. This cell contained a platinized screen auxiliary electrode oriented parallel to the painted metal surface. An aperture in the screen contained a glass-lined Ag/AgCl tipped reference electrode which was positioned between the painted surface and the counter electrode along the center line of the cylindrical cell. Impedance experiments were conducted using a Solartron 1250 frequency response analyzer, Stonehart BC 1200 potentiostat, and Tektronix 4052 computer. Impedance data were collected at frequencies ranging from 65 kHz downwards to 1 mHz.^[10]

Occasionally during the exposure, each opaque panel was characterized by electrochemical impedance spectroscopy using a clamp-on cell similar to that described above but of 13.3 cm² area. Every few months, the panels were evaluated visually using ASTM Standard D-610^[16] for rust area, and a modification to D-714^[17] for blistering. These standards rate defective area on a scale of 0-10 as illustrated in Fig. 4. Defect area percentages less than 0.01% (ASTM 10 rating) are

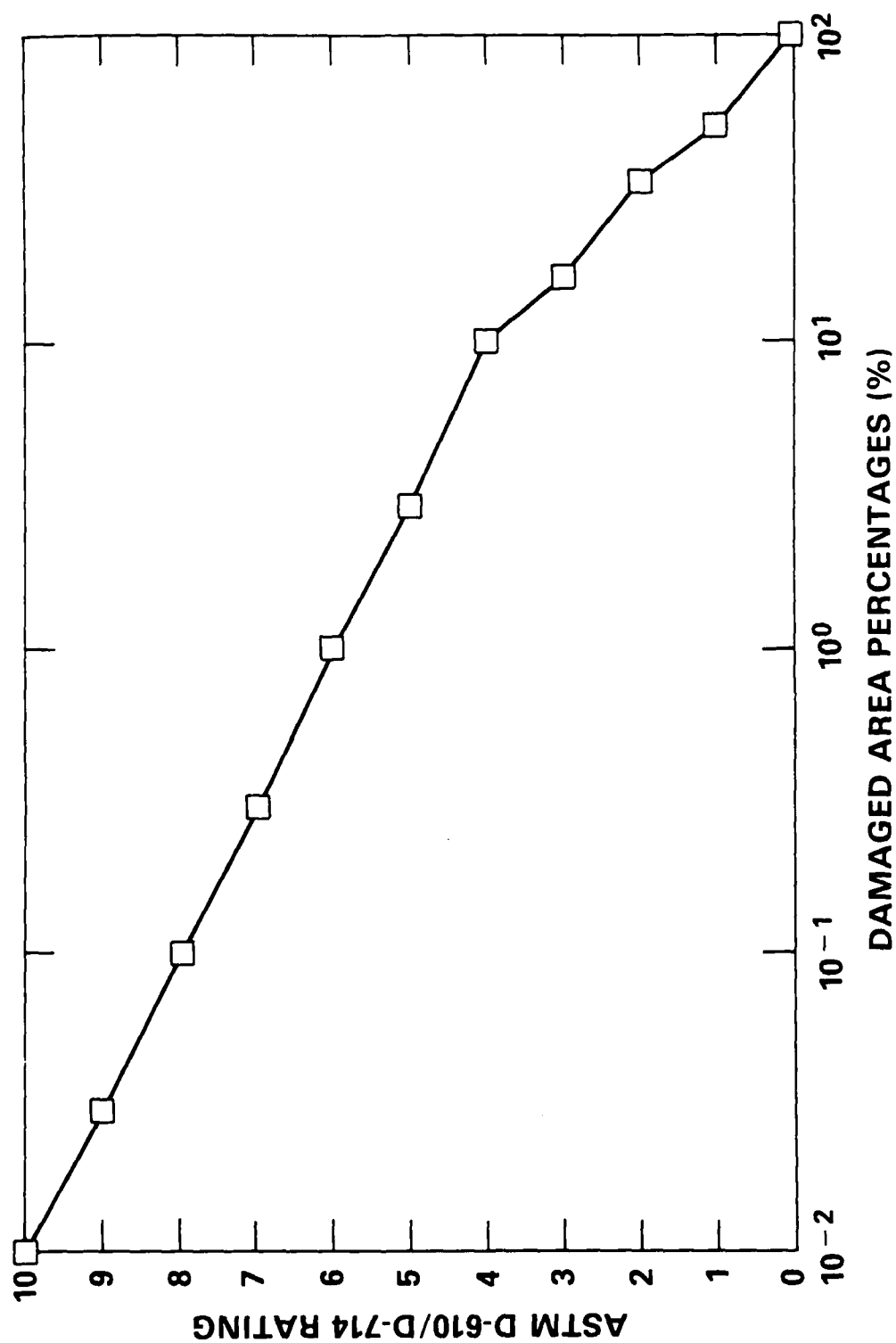


Fig. 4. Defect area percentages for 0-10 rating system for ASTM standard D-610 and modified D-714.

not considered in this system. Visual ratings on transparent coatings were used in addition to opaque coatings in order to increase the level of confidence in the ASTM visual methods.

RESULTS AND DISCUSSION

Modeling

Impedance data from the transparent coated panel, both with and without the intentional defect, are presented in Figs. 5 and 6. A very low breakpoint frequency was observed for the defect-free sample with no corrosion visible at the coating-metal interface. A very high breakpoint frequency (greater than 65 khz) was observed for the test conducted over the defect. Since these measurements were made after 3 hours exposure, no delamination is assumed to have occurred under the coating adjacent to the bare metal. The intentional defect area of 0.0066 cm² can therefore be assumed to still be accurate.

Figure 7 shows the equivalent circuit model and specific resistances and capacitances that were used to model these data. The specific resistances and capacitances, and the "defect" area for the intact coating, were obtained by fitting to the data. The result was an equivalent circuit model in which only one parameter, coating defect area, could be changed to create the two solid curves in Figs. 5 and 6. This shows that the assumed model is capable of fitting data from coatings with intentional defects. The next logical experimental step, using a range of defect sizes, was not done due to the difficulty of accurately making defects smaller than 0.0066 cm². Larger defect sizes were not used as the frequency of 45 degree phase shift was already

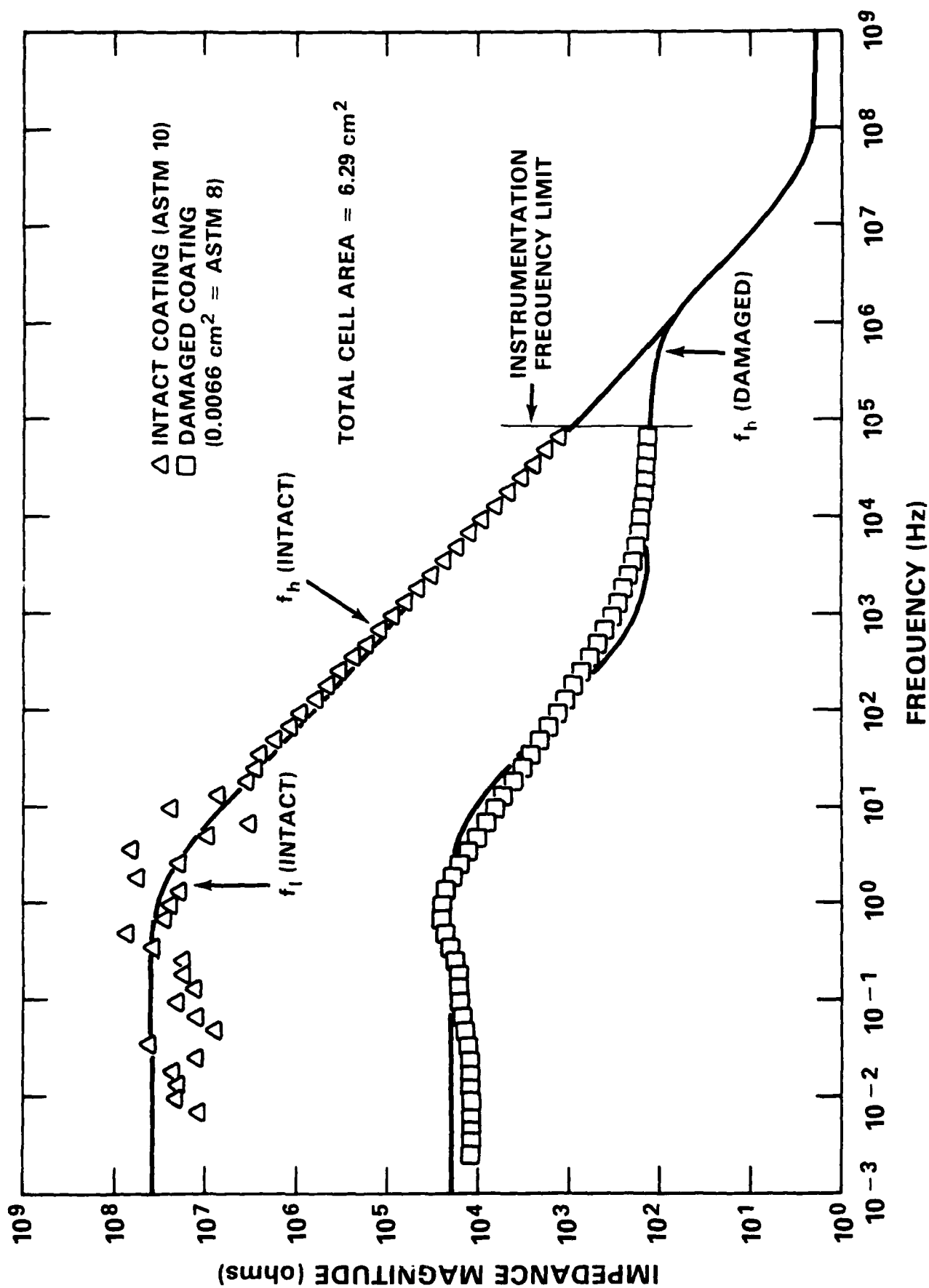


Fig. 5. Impedance magnitude data for a transparent epoxy coating on steel in ASTM seawater. Solid lines are fit from equivalent circuit model.

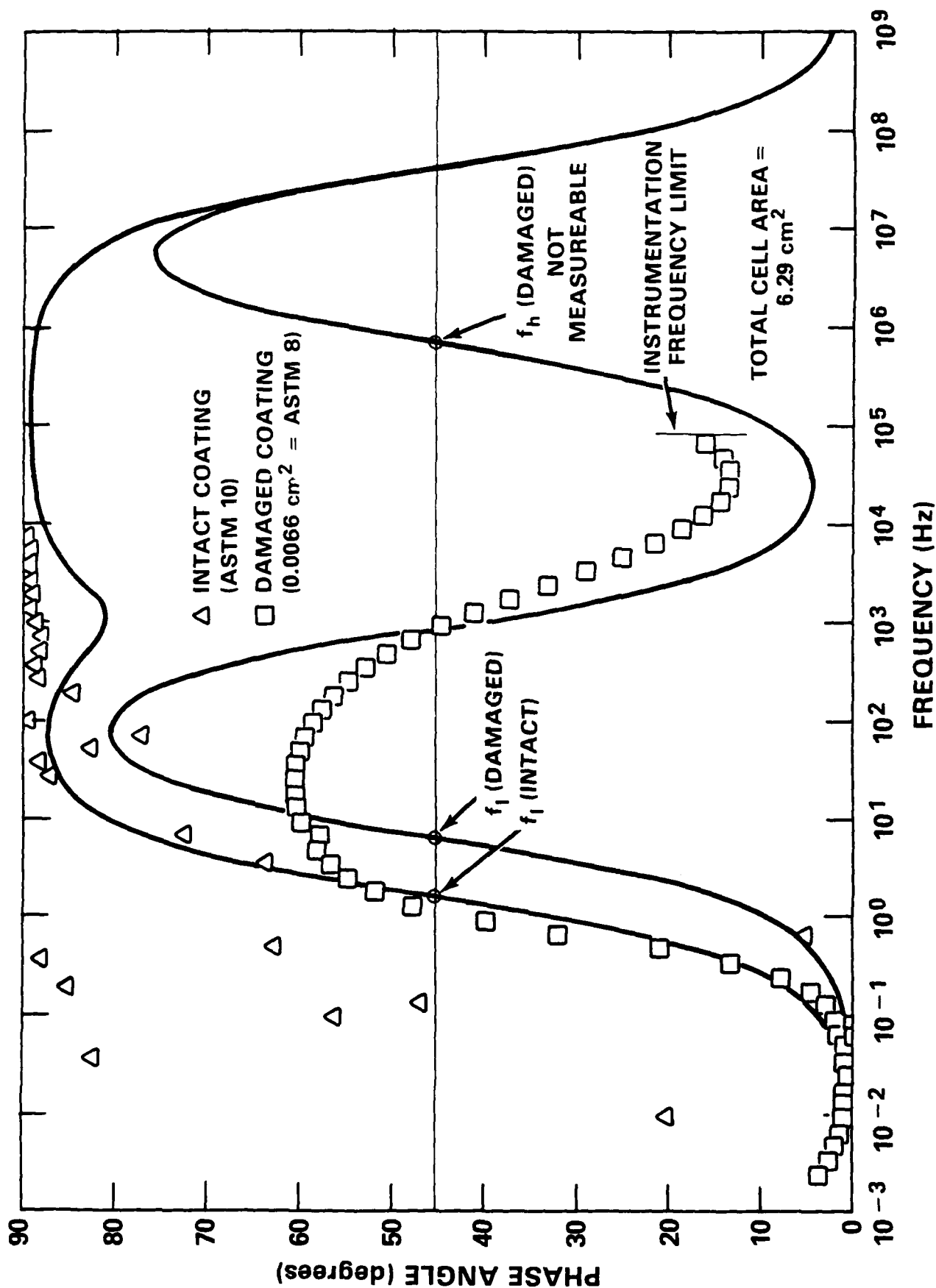


Fig. 6. Impedance phase data for a transparent epoxy coating on steel in ASTM seawater. Solid lines are fit from equivalent circuit model.

"SPECIFIC" VALUE (ASSUMED TO GET DATA FIT)	$A_{\text{cell}} = 6.29 \text{ cm}^2$	
	$A_d = 0.0066 \text{ cm}^2$	$A_d = 3.2 \times 10^{-6} \text{ cm}^2$ *
$C_c = 2 \times 10^{-9} \text{ F/cm}^2$	$C_c = 1.3 \times 10^{-8} \text{ F}$	$1.3 \times 10^{-8} \text{ F}$
$R_s = 12 \Omega\text{-cm}^2$	$R_s = 2 \Omega$	2Ω
$r_t = \frac{130 \Omega\text{-cm}^2}{A_d}$	$R_t = 2 \times 10^4 \Omega$	$4 \times 10^7 \Omega$
$r_d = \frac{1.3 \Omega\text{-cm}^2}{A_d}$	$R_d = 200 \Omega$	$4 \times 10^5 \Omega$
$C_{dl} = 1.3 \times 10^{-3} \text{ F/cm}^2 \times A_d$	$C_{dl} = 8.4 \times 10^{-6} \text{ F}$	$4.2 \times 10^{-9} \text{ F}$

* FOR INTACT COATING, ASSUMED TO GET PROPER FIT

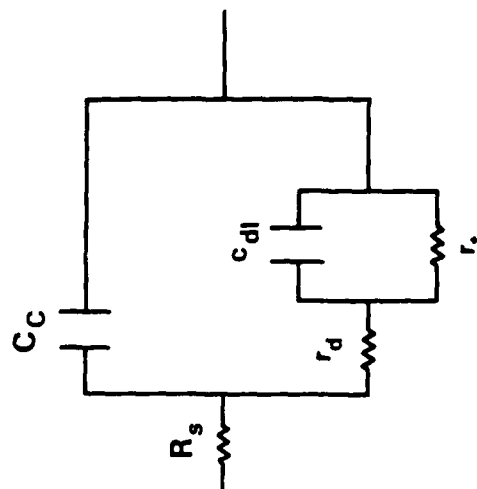


Fig. 7. Equivalent circuit components used for curves in Figs. 5 and 6.

larger than the maximum frequency of the transfer function analyzer used in gathering the data.

The difficulty in determining whether it is f_1 or f_b that is being measured can be seen to not be such a great disadvantage when inspecting Figs. 5 and 6. A coating is considered bad for marine service if it has large defects, typically larger than in these figures. Under these conditions, f_b is being measured all of the time. Thus if the breakpoint frequency exceeds the level predetermined as being "too many defects", f_b will always be the measured quantity. A better coating, with a lower breakpoint frequency, may still suffer the ambiguity, but this will be irrelevant in practice, since the coating is likely to be acceptable from a practical standpoint. Also, as mentioned earlier, there is a range of breakpoint frequencies that theoretically will not be measured, although in practice these frequencies are seen.

Comparison of ASTM ratings and defect area percentages from breakpoint frequency measurements in Figs. 2, 3, 5, and 6 show that the breakpoint frequency method can show differences in coating performance even for coatings with ASTM visual ratings that have not fallen below 10. This is therefore a very sensitive and useful technique for studying the early stages of coating breakdown.

Relationship Between Breakpoint Frequency and Exposure Time

Figures 8 to 11 illustrate the behavior of 25, 55, 116, and 155 μm thick opaque epoxy polyamide coatings on steel, respectively. From these figures the difficulty in extracting capacitance data can be seen, since high enough frequencies cannot be reached to obtain a segment of

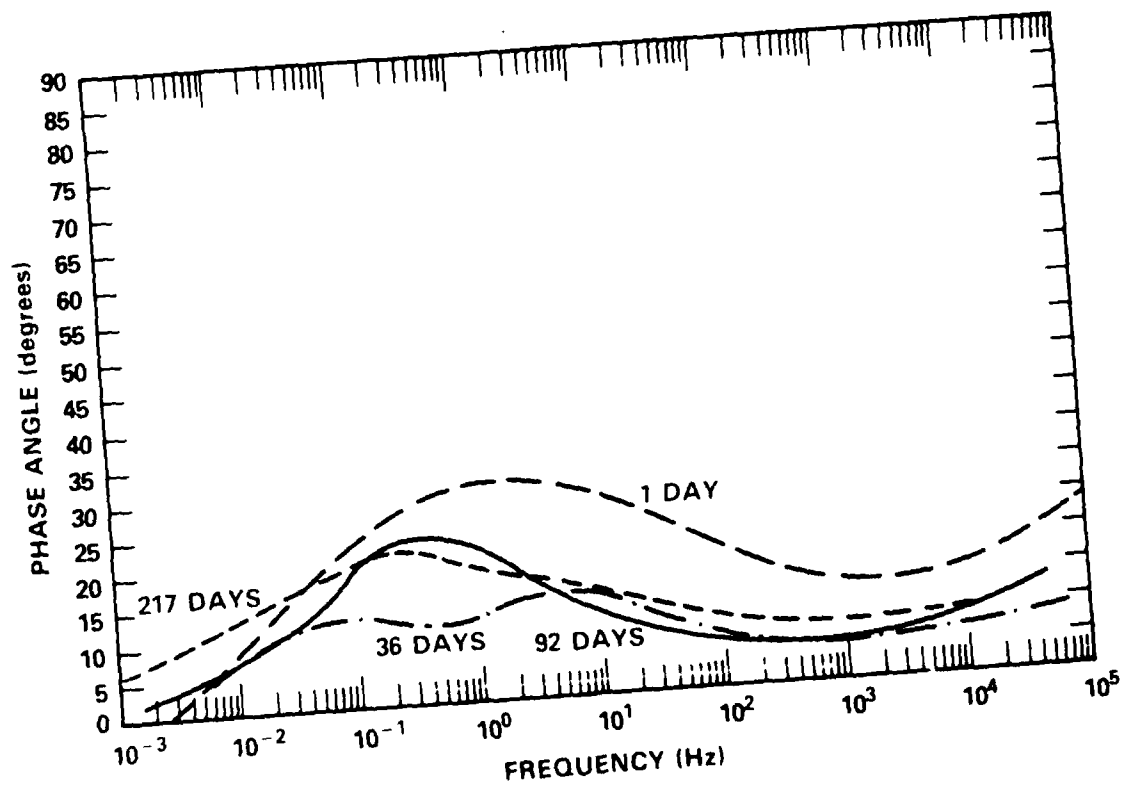
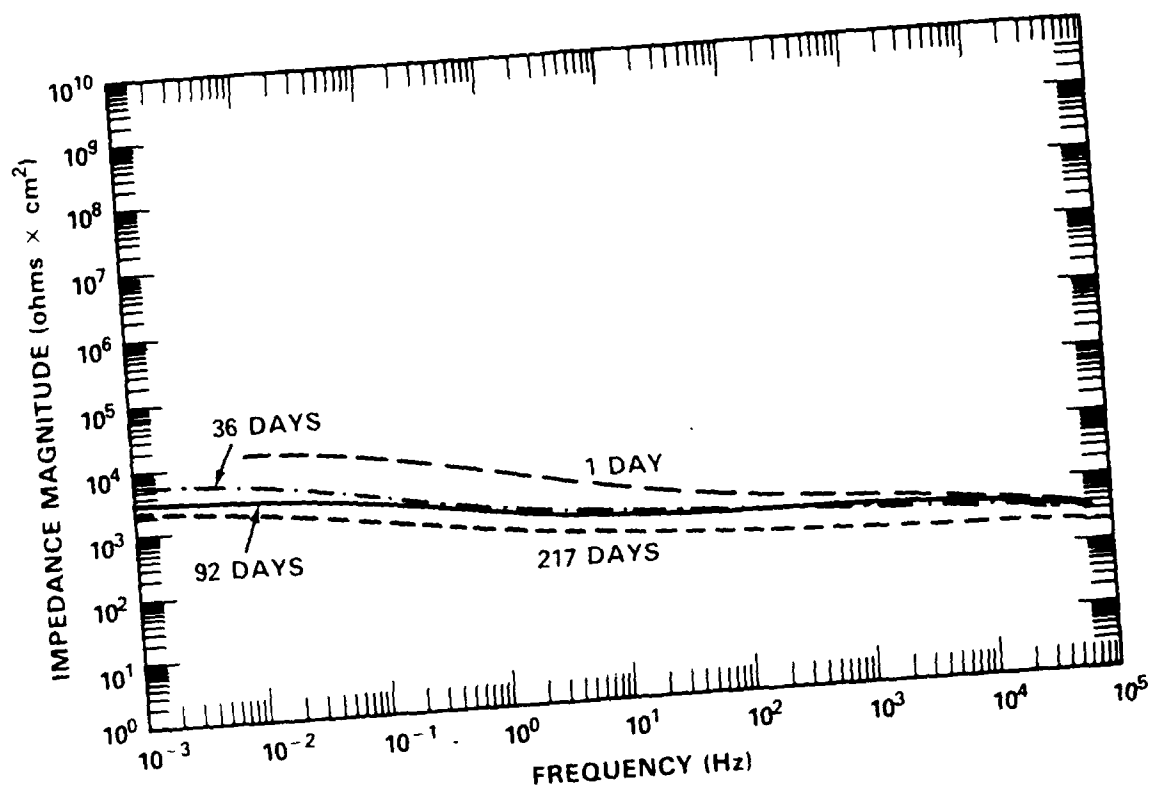


Fig. 8. 25 μ m thick epoxy coating on steel after various exposure times in seawater. (Area 13.13 cm²).

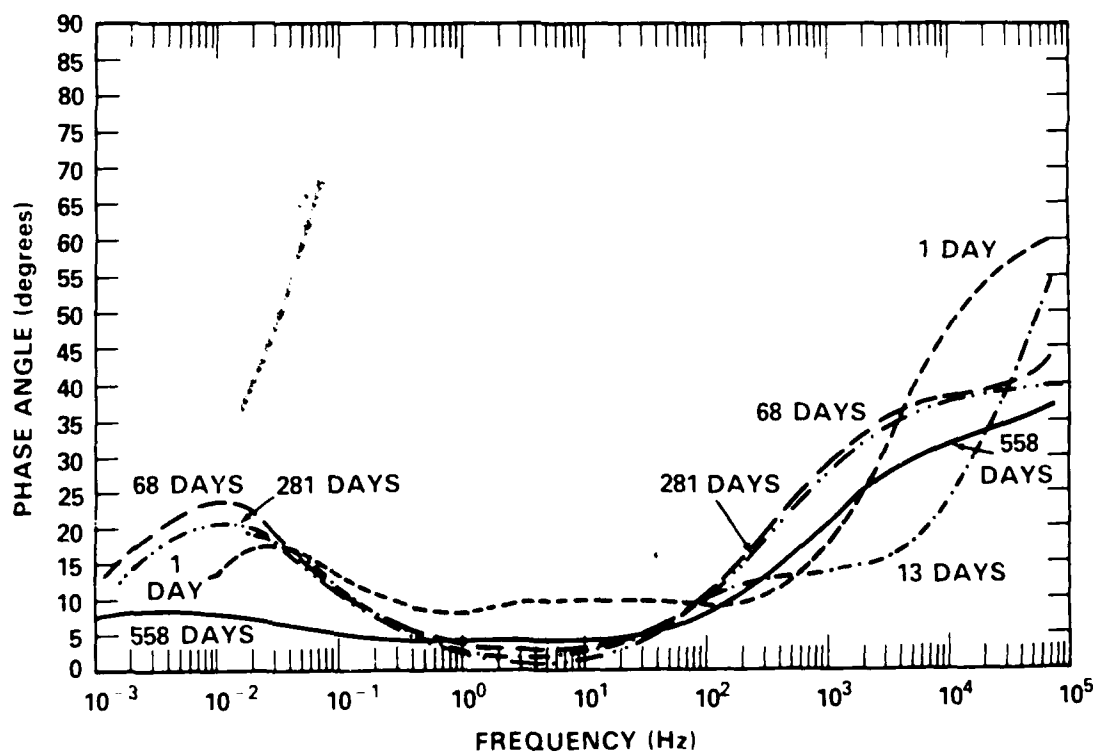
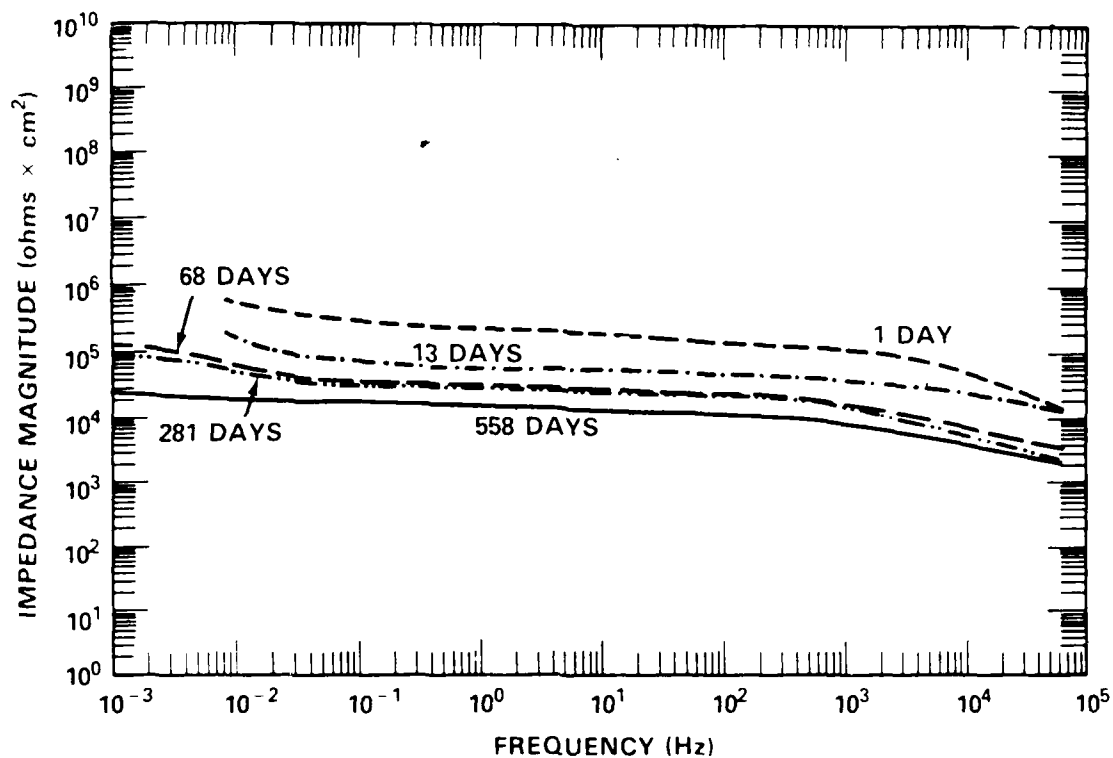


Fig. 9. 55 μ m thick epoxy coating on steel after various exposure times in ASTM seawater. (Area 13.13 cm²).

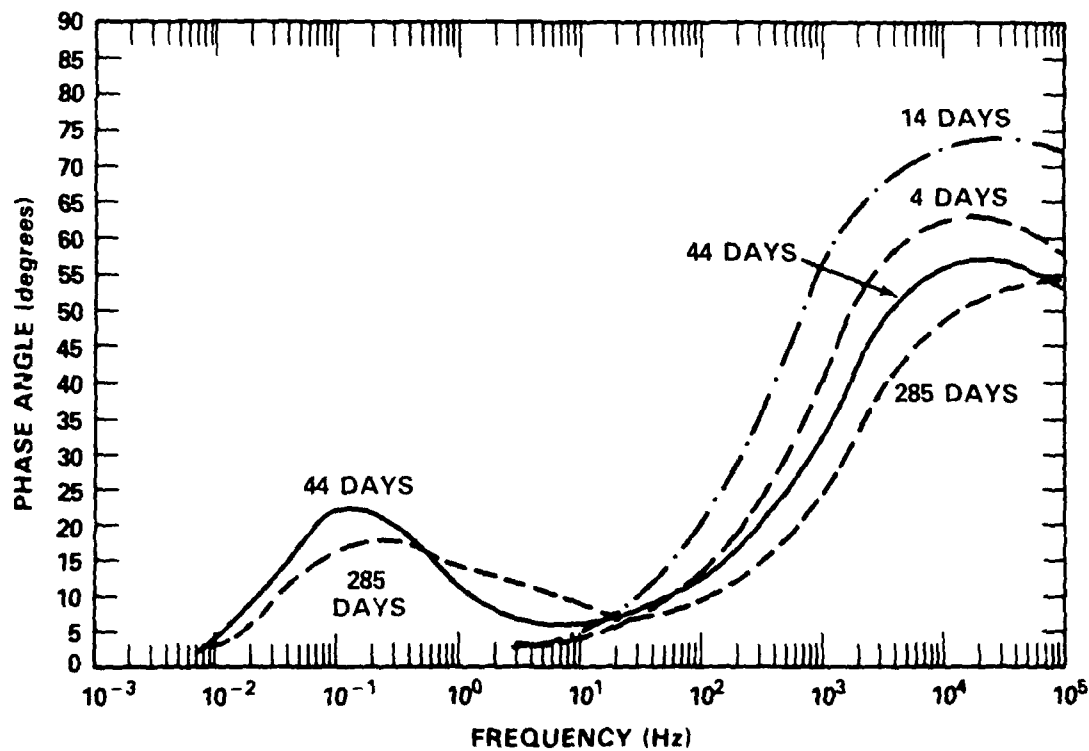
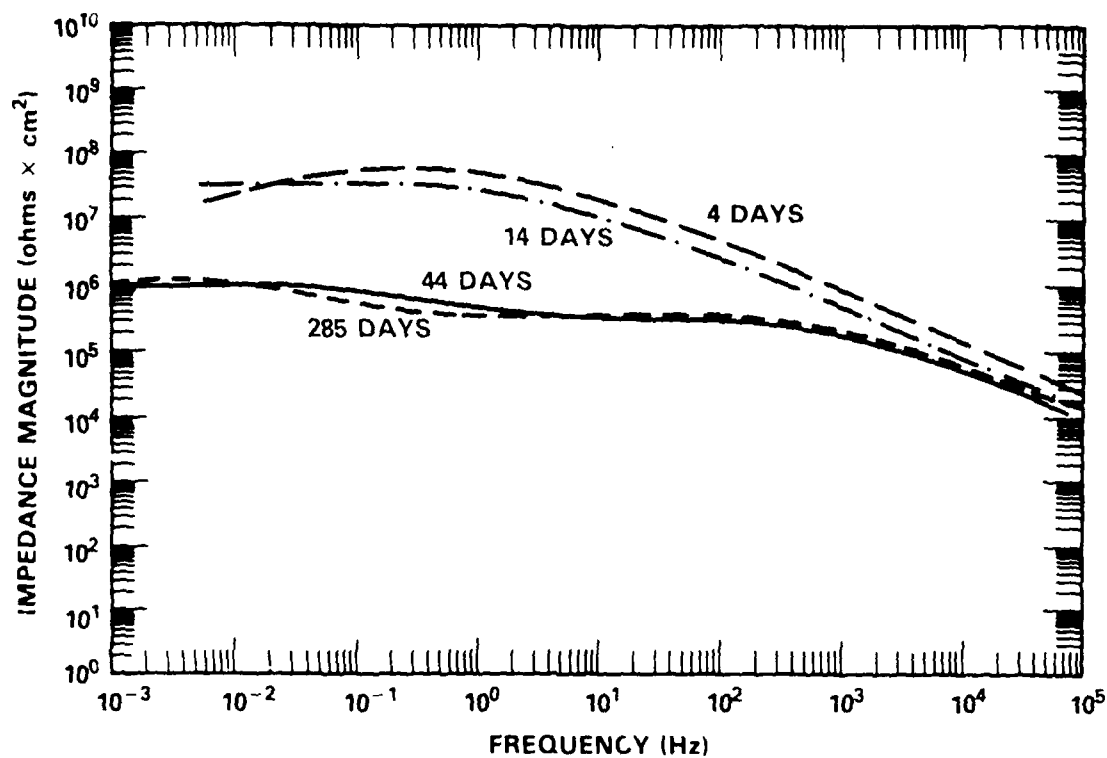


Fig. 10. 116 μm thick epoxy coating on steel after various exposure times in ASTM seawater. (Area 13.13 cm^2).

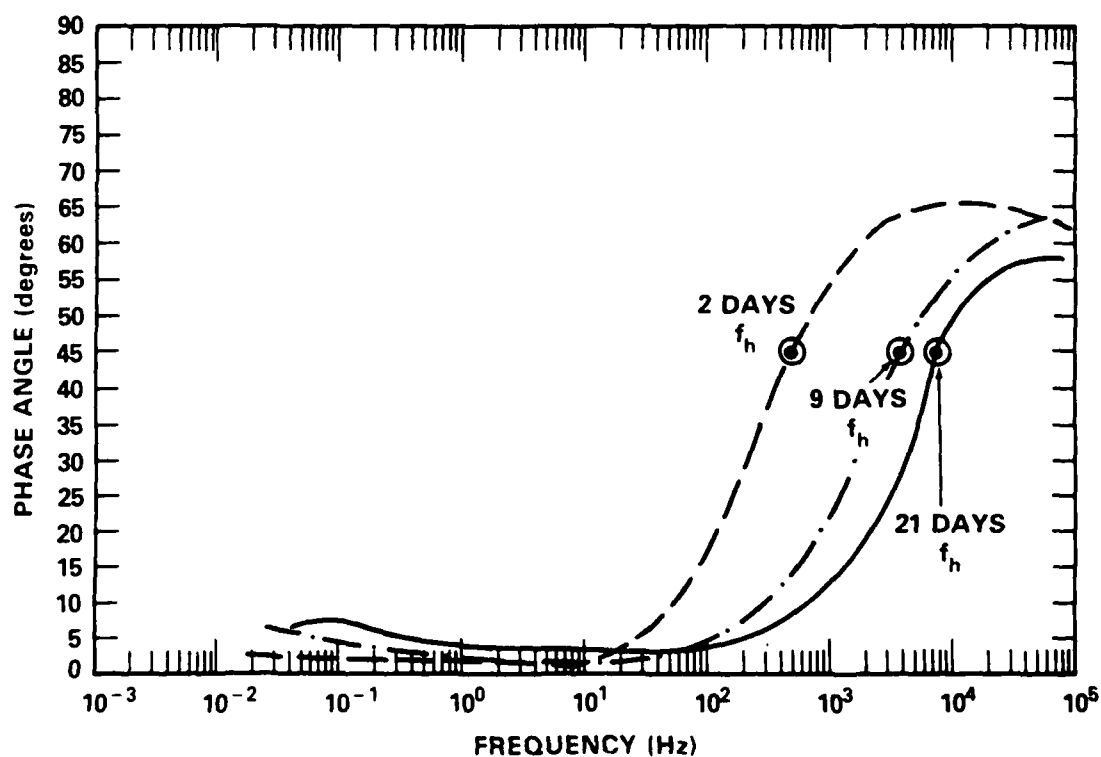
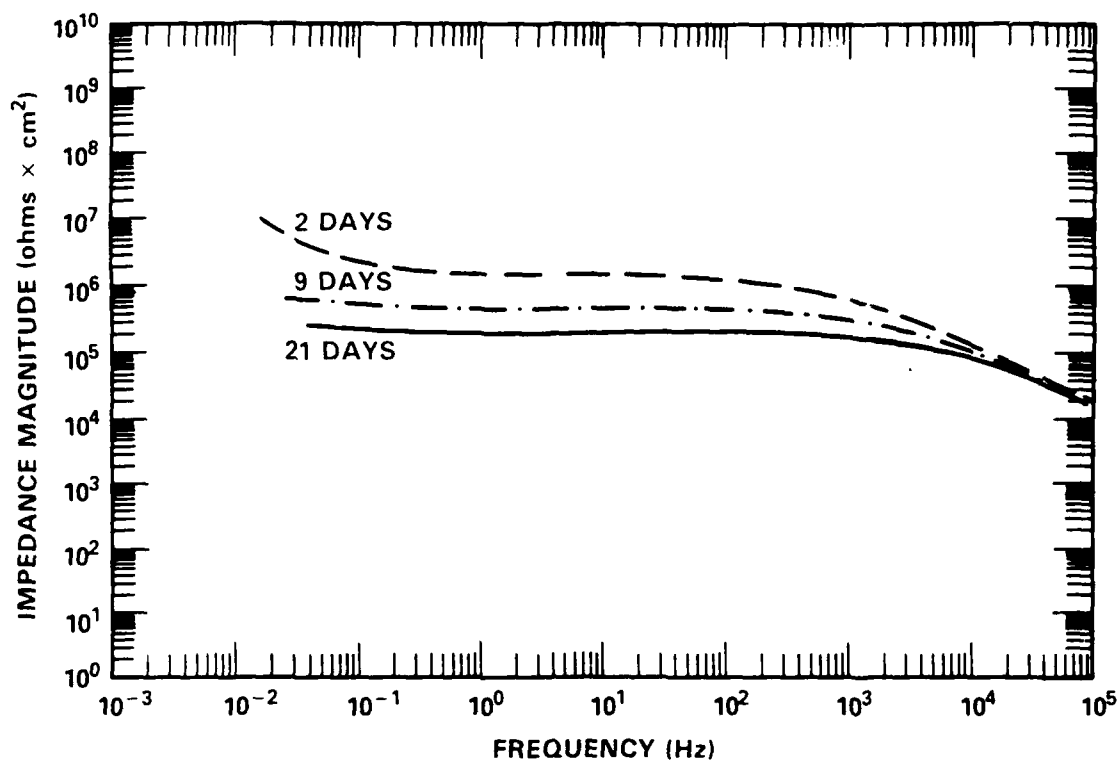


Fig. 11. 155 μ m thick epoxy coating on steel after various exposure times in ASTM seawater. (Area 13.13 cm²).

curve with -1 slope. This is contrasted to the ease in determining the breakpoint frequency. The 25 μm thick coatings displayed evidence of corrosion within several days, and their breakpoint frequency is greater than 65 KHz at all exposure times. The 55 μm coating exhibited breakpoint frequency increases from about 10^4 Hz at day one to over 65 kHz by 558 days. The 155 μm thick coating showed an increase in the breakpoint frequency which was accelerated over 21 days by cathodic polarization. The 25 and 55 μm thick coatings had greater breakpoint frequencies at all times than the 116 and 155 μm thick coatings, consistent with the greater amount of corrosion and blistering observed. In all cases the frequency associated with the 45 degree phase angle increases with exposure time, as shown in Figs. 12 and 13 for two replicate 55 μm and 155 μm thick coatings, respectively. The ASTM visual ratings are also shown on these plots. Good correlation between visual corrosion and the breakpoint frequency is observed.

Figure 14 shows the relationship between breakpoint frequency and estimated active area for both opaque and transparent coatings. The solid lines outline the scatterband for the data, with the expected slope of 1 for a proper correlation. The same trend is observed for the transparent coatings as for the opaque coatings. A breakpoint frequency greater than 10^4 Hz indicates an active area equal to or greater than about 0.01%. A frequency less than 10^2 Hz indicates an active area equal to or less than about 0.0001%. The large amount of scatter in the data could be due to the uncertainties associated with estimating active area by visual means. Rust staining on the transparent coatings may remain visible even after corrosion has subsided, contributing to the

data scatter. Other methods for estimating active area such as acoustic or infra-red microscopy may prove more accurate.

Two-electrode measurements

The impedances involved on the coated surfaces are much higher than those of some counter electrodes. A two-electrode impedance measurement without a reference electrode measures the sum of counter and working electrode impedances. When the counter electrode impedance is negligible compared to that of the working electrode, these two techniques give the same results. Thus, a two-electrode system could be used for coating measurements, making the use of a potentiostat unnecessary. This would allow the measurement frequency to be extended well above the 65 KHz used in this study, increasing accuracy for large defect sizes.

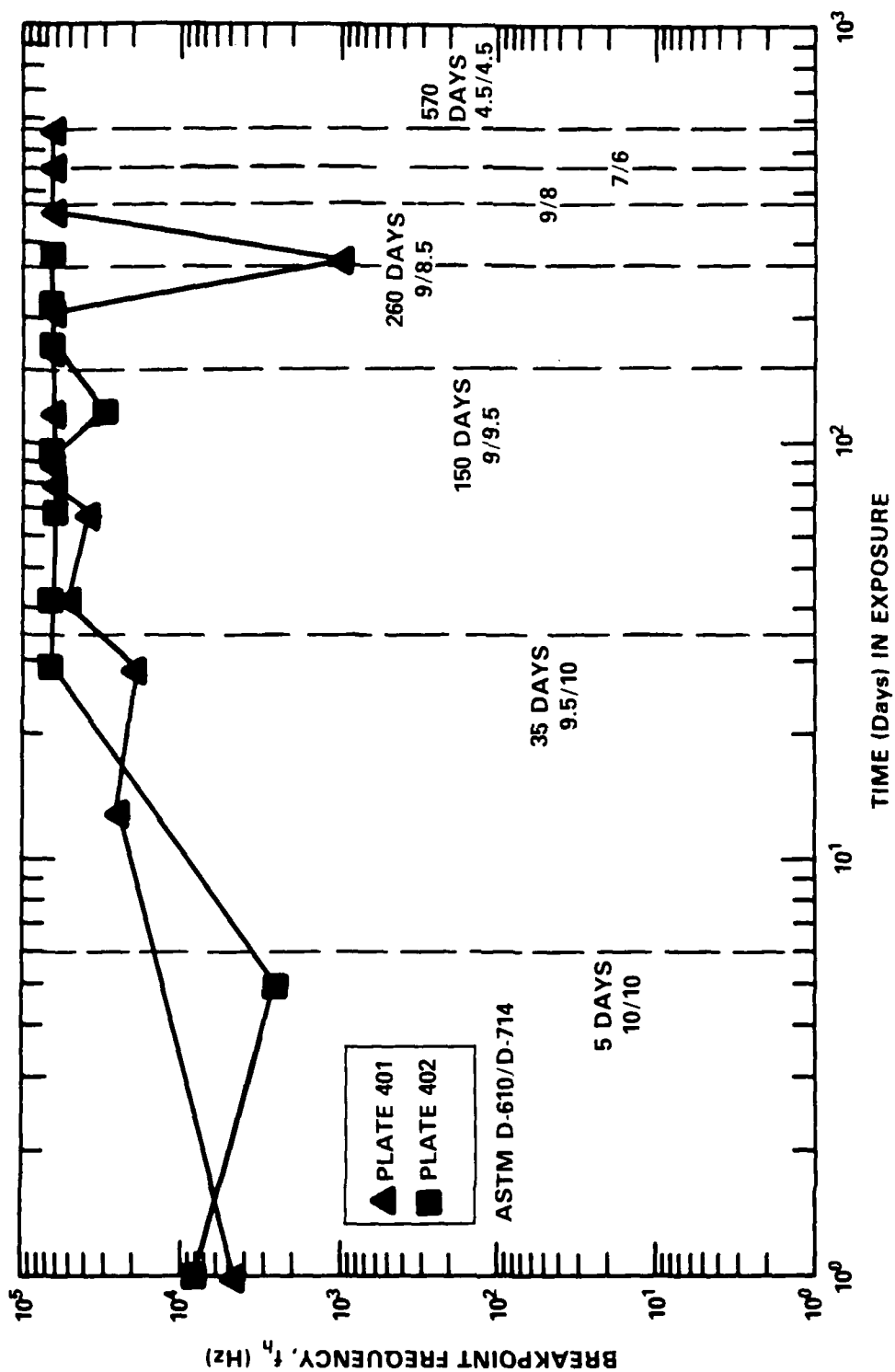


Fig. 12. Increase in the higher breakpoint frequency with exposure time for 55 μ m thick epoxy coated steel in ASTM seawater. (Area 13.13 cm^2).

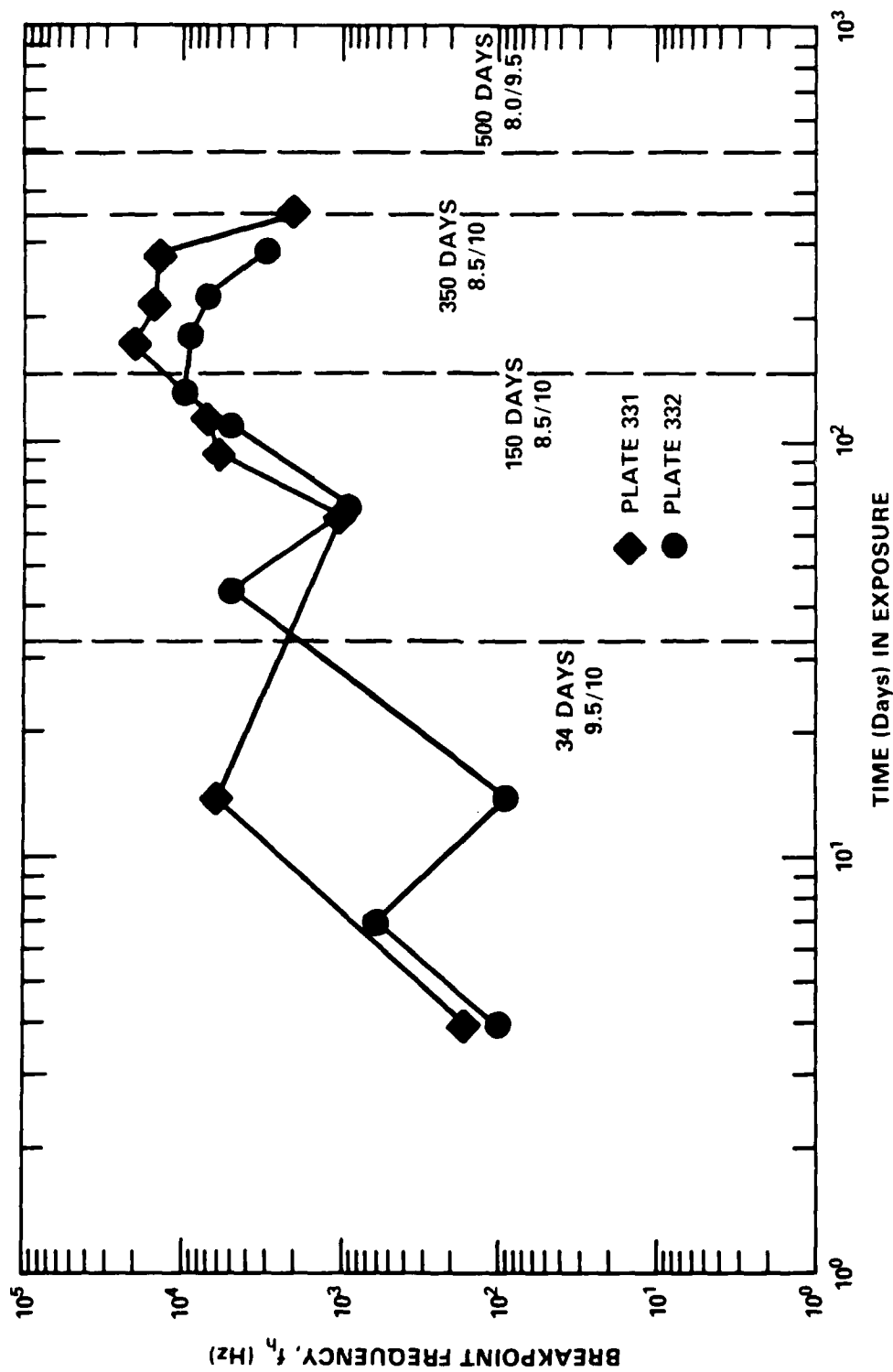


Fig. 13. Increase in the higher breakpoint frequency with exposure time for 116 μ m thick epoxy coated steel in ASTM seawater. (Area 13.13 cm^2).

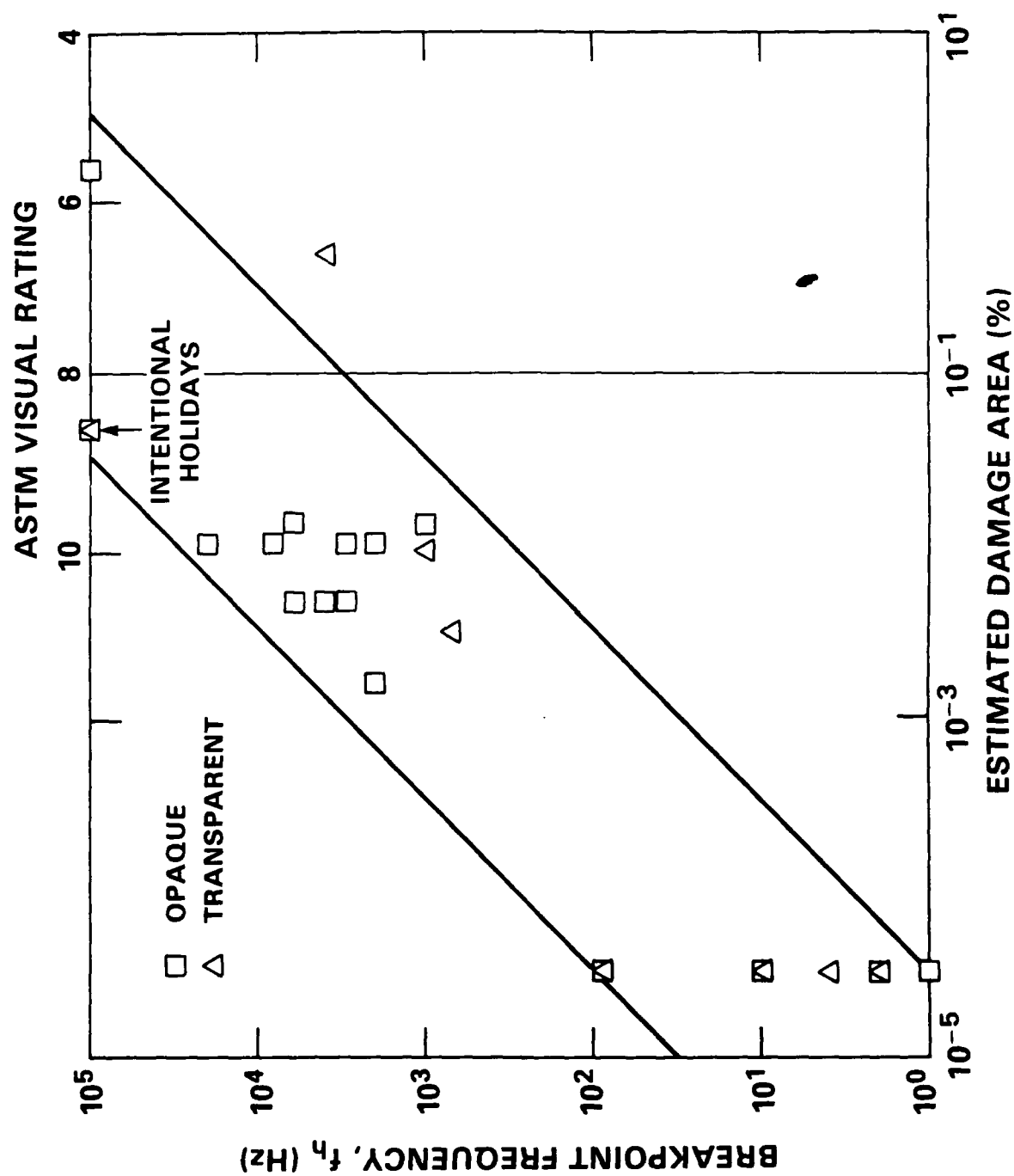


Fig. 14. Relationship between breakpoint frequency and estimated electrochemically active area for opaque and transparent epoxy coatings on steel.
(Solid lines have been added to aid the reader)

CONCLUSIONS

The purpose of this work was to evaluate the breakpoint frequency approach to determining coating defect area for use by the Navy for ship coating systems. This method was found to be extremely useful in this regard.

The equivalent circuit model used in the breakpoint frequency analysis is capable of fitting actual data on coated steel panels with and without an intentional defect. A correlation was obtained between the breakpoint frequency and visually estimated electrochemically active area on epoxy coatings of a variety of thicknesses. This approach offers a simple alternative to determination of defect areas via the use of the pseudocapacitance from difficult to analyze low frequency impedance data. This approach also can detect the beginnings of coating breakdown long before visual indications are present. A simple two-electrode setup without a potentiostat could be used over a larger range of frequencies to generate more accurate information for larger defect sizes.

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