

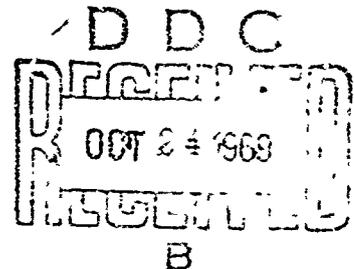
**Corrosion Analysis of 304 Stainless Steel Wire Rope
and Fittings From a NOMAD Buoy Mooring System
After 34-Months Continuous Service
in the Gulf of Mexico**

AD695372

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Abstract

Samples from a 1250-ft length of 304 stainless steel wire rope and associated stainless steel tube thimbles and stainless steel cable clamps were studied to determine the extent of corrosion after 34-months continuous immersion in the Gulf of Mexico. This 3/4-in.-diam wire rope (6 x 19 Warrington - IWRC 7 x 7) was used in the upper portion of a Nomad buoy mooring system. The performance of this particular buoy design is important because of its possible influence on the national buoy program.

The absence of any significant corrosion on the top 1000 ft of this stainless steel wire rope was attributed to the beneficial effects of the retained lubricant, to the cathodic protection from a steel anode located just above the wire rope, and to probable inadvertent cathodic protection from the 6061-T6 aluminum surface buoy.

The lower 250 ft of the wire rope was jacketed with neoprene to prevent abrasion of the synthetic rope used for the lower section of the mooring system. The distance from the anode and the electrical shielding effect of the jacket prevented effective cathodic protection of this section of the rope, and relatively severe corrosion was observed.

Experience gained in this stainless steel wire rope analysis and other wire rope corrosion analyses currently being conducted indicates that one cannot determine the extent of corrosion of wire ropes by an inspection of only the exposed external surfaces. This is especially true when a material such as the common grades of stainless steel is used because the corrosion of such material occurs locally by tunnelling or crevice corrosion or pitting and, therefore, may not be evident externally. For certain critical applications, i.e., where the system is not extremely over-designed, it may be necessary to replace the wire rope at the first sign of rope deterioration as evidenced by rusting or whiskering.

Status

This report completes one phase of the task; work is continuing on other phases.

Authorization

NRL Problem No. 63M04-02
Tasks SF 51-542-602-12431 and S-4607-11894

INTRODUCTION

Because of the increased use of moorings to lower and secure instrument packages and buoys in deep areas of the ocean, the Marine Corrosion Section of the Naval Research Laboratory's Metallurgy Division has been concerned with the corrosion performance of the various types of metallic wire ropes used for such moorings. An analysis of the failure of AUTECH TOTO II deep sea moor and of the performance of its cathodic protection system was reported by Groover (1). The AUTECH moor was a three-legged moor and used 1 1/4-in.-diam 6 x 19 filler wire (WSC), extra-improved plow steel, galvanized, bituminous-coated wire rope. A limited-size cathodic protection system of magnesium anodes was designed by NRL and installed to protect critical junctions of the moor. The service life of the TOTO II moor was approximately 4 1/2 years in 5000 ft of seawater in the Tongue of the Ocean (TOTO) area of the Bahama Islands.

The Nomad buoy moor discussed in this report and located in the Gulf of Mexico (lat 25-00N, long 90-00W) was recovered in April 1969 after 34-months continuous service. This moor was under the cognizance of the Naval Weapons Quality Assurance Office - Meteorological Instrumentation Division - QAO-56. The Nomad buoy has nominal dimensions of 20 x 10 x 8 ft, displaces approximately 10 tons, and has a loaded draft of 7 ft. It was fabricated from 6061-T6 aluminum and was intended to be isolated from the mooring with phenolic insulators.

The general design drawings for the Nomad buoy mooring system showed approximately 15 ft of 3/4-in. stainless steel chain directly beneath the buoy but isolated from it and approximately 1000 ft of 3/4-in.-diam stainless steel wire rope below the chain. An iron anode was included in the moor design for cathodic protection purposes. The anode for this system was located near the top of the moor in the chain section. The construction of the wire rope on the Nomad buoy moor studied was 6 x 19 Warrington (IWRC 7 x 7). The general design also showed the lower end of the stainless steel wire rope to be covered by a 200-ft. length of fabric or rubber hose. A neoprene jacket covered the lower 250 ft of the 304 stainless steel wire rope of the Nomad buoy moor discussed in this report.

A 7/8-in.-diam plaited dacron or polypropylene rope below the stainless steel wire rope was shown in the general Nomad buoy moor design. The fabric or rubber hose on the stainless steel

steel wire rope was specified to prevent chafing of the synthetic rope by the stainless steel if at times the synthetic rope was not taut and rose toward the surface.

Previous studies (2,3) have shown very severe corrosion of 304 stainless steel in seawater unless the specimens or structures were receiving cathodic protection, hence the interest in a buoy which may influence the design of "standard" buoys and which afforded an opportunity to observe stainless steel wire rope after 34-months continuous immersion in seawater.

PROCEDURES

On 12 June 1969, NRL personnel visually inspected the approximately 1250 ft of 304 stainless steel wire rope from the Nomad buoy mooring system at the Washington Navy Yard. Specimens for the corrosion study were selected from locations along the wire rope which the visual inspection indicated would be representative of the wire rope's condition. The locations from which the specimens were removed for the corrosion study are shown in Table 1. Simultaneously, Mr. Norbert Rendler (NRL Code 8444) removed samples adjacent to the corrosion specimens in order to study the mechanical properties of the wire rope. The study on mechanical properties of this wire rope will be covered in a separate report by Code 8444.

Products on the wire rope were removed from selected locations for spectrographic analysis and possible identification by x-ray diffraction. Approximately 3 to 4-in. lengths from each sample location were alternately delubricated with toluol in an ultrasonic bath and chemically cleaned in 10 percent HNO_3 at 60°C prior to the microscopic examination. The microscopic study included a detailed examination of many of the individual wires (usually all the wires in one outer strand and the IWRC of each selected length). Cross sections of all the wire rope specimens were prepared metallographically for study. Micrometer measurements were also obtained on the diameter of individual wires of each specimen.

CORROSION ANALYSIS AND DISCUSSION

The corrosion analysis of the stainless steel wire rope specimens and fittings have been summarized in Tables 1 and 2, respectively. A description of the appearance of the wire rope at various distances from the top, corrosion observations on the cross-section specimens at 30X magnification, x-ray diffraction identification of products on the wire rope surfaces at selected locations, observations on the overall appearance of individual

wires, and a qualitative summary of the extent of corrosion have been included in Table 1.

Products on the Wire Rope Surfaces

When a metal has been cathodically protected in seawater and certain conditions of temperature and potential achieved, the protected metal (the cathode) will have developed films on its surface. These films consist mainly of calcium and magnesium salts and have been called calcareous deposits. In some areas of the ocean similar white deposits which are unrelated to the cathodic protection process may also be formed on metal surfaces. Such deposits have often been called "marl" and have resulted from marine-life decay. However, the origin of the deposit can be determined by x-ray diffraction techniques.

The visual inspection of the stainless steel wire rope showed a white product on its surfaces to a distance of slightly over 100 ft from the top. X-ray diffraction analysis identified CaCO_3 (calcite) as a major constituent of these products to a distance of 13 ft from the top, and calcite as a minor constituent to a distance of 104 1/2 ft. $\gamma\text{FeO(OH)}$ was also identified in the products sampled at the 11 to 13-ft. distance. Microscopic examination of this section of wire rope showed essentially no corrosion (Fig. 1). The presence of $\gamma\text{FeO(OH)}$ at this relatively short distance from the top of the wire rope was believed to be the result of corrosion of the iron anode which was installed above this location for cathodic protection purposes. Spectrographic analysis of the products on the wire rope at the 11 to 13-ft distance showed very strong lines for Ca, Mg, Si, and strong lines for Al. The presence of aluminum and the CaCO_3 (calcite) indicated that the wire rope was not only being cathodically protected by the iron anode, but the aluminum buoy probably was not isolated from the mooring for at least a portion of the exposure time. The aluminum hull buoy probably furnished additional cathodic protection to the wire rope.

Products on the stainless steel wire rope at the 1231 ft to 1233-ft distance from the top were mainly $\gamma\text{FeO(OH)}$ and $\alpha\text{FeO(OH)}$. Spectrographic analysis of the products at this location gave strong lines for Cr, Ni, and very strong lines for Fe. The presence of these elements and the iron compounds above was consistent with the corrosion of 304 stainless steel which was a chromium-nickel-iron alloy. Strong lines for Ca and Mg were also detected spectrographically on this specimen, but reasons for their presence were not known. Compounds that contained these elements were not identifiable by x-ray diffraction which

indicated either that their concentration was quite low or that they were amorphous.

During cleaning of the wire rope sections for microscopic examination, considerable lubricant was still evident between individual wires. In order to adequately clean the specimens for detailed examination it was necessary to alternately immerse them in toluol in an ultrasonic bath and in 10 wt-percent HNO₃ at 60°C. A relatively large quantity of lubricant was apparently retained in this stainless steel wire rope during its 34-month exposure.

Corrosion Observations and Data

Wire Ropes -- Observations and data on the condition of the 304 stainless steel wire rope moor of the Nomad buoy have been assembled in Table 1 and Figs. 1 through 5. There was essentially no corrosion to a distance of approximately 520 ft from the top of the wire rope. The essential absence of corrosion has been exemplified in Fig. 1 which is a typical photograph of this condition. The relatively excellent condition of the wire rope to the 520-ft distance was attributed to the retained lubricant and to cathodic protection from the purposely installed iron anode and the apparently inadvertent cathodic protection from the aluminum buoy.

The outward visual appearance of the wire rope was similar between 520 ft and 1000 ft, and therefore no samples were taken in this span.

A definite transition was visually apparent between 1005 ft and 1009 ft. This transition was a change from a dark surface film to a heavily rusted condition beneath the neoprene jacket which covered the bottom 250 ft (approximately) of the wire rope. Only slight corrosion was observed just above and 4 in. outside the neoprene jacket. The condition of the wire rope at the rusted end of the transition area has been shown in Fig. 2.

As would be expected when 304 stainless steel was shielded and not effectively cathodically protected, the corrosion under the neoprene jacket was quite severe. The tunnelling (black areas in cross-section photographs), deep pitting, and crevice corrosion that occurred on individual wires located between 1009 ft and 1233 ft from the top have been shown in Figs 3, 4, and 5. This tunnelling, deep pitting, and crevice corrosion was typical for 304 stainless steel corrosion in quiescent seawater.

Fitting Areas of Wire Rope and Fittings -- The corrosion observed on the wire rope under the 304 stainless steel cable clamps has been described in Table 1. The corrosion was much more severe on the shielded (with tape) areas at the lower end of the wire rope compared to the areas near the top of the mooring which were unshielded and received cathodic protection. A comparison of the extent of corrosion that occurred at these areas is indicated in Figs. 6 and 7. The severe pitting and crevice corrosion observed on the wire rope under one of the lower cable clamps are indicated in Fig. 8.

The overall condition of the upper and lower 304 stainless steel fittings, i.e., cable clamps, clamp nuts, and tube thimbles was generally excellent. Some shallow pitting had occurred, however, on the base metal of the tube thimble in the heat-affected zone caused by the welding of a wear plate to the tube thimble. A crack was also evident at the junction of the weld and the tube thimble located at the top of the stainless steel wire rope. This crack may have been caused by a cold weld or by uncutting during welding. The cracked area before and after electrolytic etching in 10 percent oxalic acid is shown in Fig. 9.

Wire Diameters -- The individual wire diameters of the sample from the 11 ft to the 13-ft distance from the top of the wire rope where essentially no corrosion was observed were as follows:

<u>Wire Location</u>	<u>Individual Wire Diameters (mils)*</u>
Outer Strand	
Outer Wires	41 and 54
Inner Wires	54
Center Wire	54
IWRC	
Outer Strand	
Outer Wires	32
Center Wire	32
Center Strand	
Outer Wires	35
Center Wire	35

* 1 mil = 0.001 in.

Diameters of wires from specimens taken at the various distances from the top of the wire rope were within plus or minus 1 mil of the values measured at the 11 ft to 13-ft distance as shown above. These types of general corrosion data were not unusual for stainless steel in seawater. Stainless steel generally has corroded locally by pitting or crevice corrosion in quiescent seawater. General corrosion data have, therefore, not been found significant in determining the life expectancy of stainless steel hardware in seawater.

SUMMARY

The overall corrosion of the 304 stainless steel wire rope of the Nomad buoy moor was relatively minor considering its 34-months service in seawater. The relatively good condition of this wire rope can be attributed to the beneficial effects of the retained lubricant, the cathodic protection from the steel anode, and probable inadvertent cathodic protection from the aluminum buoy.

Shielding of the lower end of the stainless steel wire rope to prevent chafing of the synthetic rope in the system caused the most serious corrosion to occur at these shielded areas. The retained lubricant and any cathodic protection that might have been afforded the stainless steel wire rope at the shielded areas were insufficient to prevent the relatively serious corrosion that was observed under the neoprene jacket.

Experience gained in this stainless steel wire rope analysis and other wire rope corrosion analyses currently being conducted indicates that one cannot determine the extent of corrosion of wire ropes by an inspection of only the exposed external surfaces. This is especially true when a material such as the common grades of stainless steel is used because the corrosion of such material occurs locally by tunnelling or crevice corrosion or pitting and, therefore, may not be evident externally. For certain critical applications, i.e., where the system is not extremely over-designed, it may be necessary to replace the wire rope at the first sign of rope deterioration as evidenced by rusting or whiskering.

ACKNOWLEDGMENT

Support of this research by the Naval Ships System Command and the Deep Submergence Systems Project Office of the Department of the Navy is gratefully acknowledged.

REFERENCES

1. R. E. Groover, "Analysis of the Failure of AUTECH TOTO II Deep Sea Moor and the Performance of Its Cathodic Protection System," NRL Memorandum Report 1950, November 1968
2. M. H. Peterson and T. J. Lennox, Jr., "The Corrosion Behavior of Stainless Steels in Sea Water," NRL Memorandum Report 1795, June 1967
3. T. J. Lennox, Jr., M. H. Peterson, and R. E. Groover, "The Corrosion Characteristics and Response to Cathodic Protection of Several Stainless Steel Alloys in Quiescent Sea Water; with a Partially Annotated Bibliography (Sixth Interim Report of Progress)," NRL Memorandum Report 1948, November 1968

Table 1
Observations on 304 Stainless Steel Wire Rope
(6 x 19 Warrington - IWRC - 3/4 in. Diam)
Nomad Buoy Moor - 34 Months Continuous Service

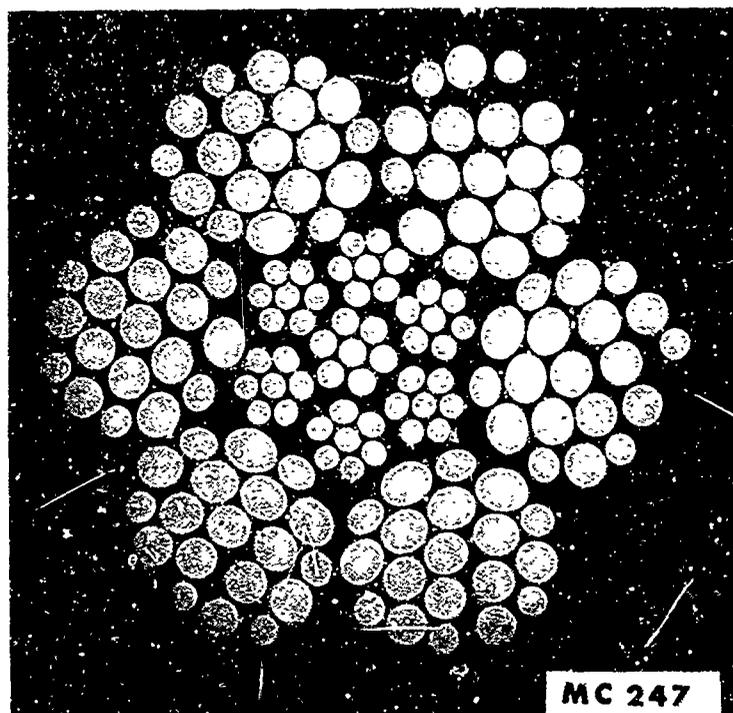
Specimen Locations Distance from Top of Wire Rope	Initial Visual Appearance of Wire Rope After Exposure	Corrosion Observations in Cross Sections (30x Magnification)	X-ray Diffraction Identification of Products On Wire Rope Surface		Overall Corrosion Observations on 3 in. Lengths of Individual Wires (20x Magnification)						Qualitative Summary			
			Major Constituents	Minor Constituents	Outer Strand		Inner Wires	Center Wire	Outer Strand (See Fig. 7)	Inner Strand				
					Large	Small								
0-11'	white deposits (on wire rope fibrous and crystalline)	---	---	---	---	---	---	---	---	---	---	---	---	
0-11'	white deposits (fibrous and crystalline)	some evidence of slight irregular corrosion	some evidence of slight irregular corrosion	---	---	---	---	shallow pitting but considerably less compared to top of cable clamp area at depth	---	---	---	---	---	
11'-13'	white deposits on top of above, but smaller fibers	essentially no corrosion	essentially no corrosion	---	---	etches								
102'4"-104'9"	end of white deposits similar to above but smaller fibers	irregular corrosion on one small wire	essentially no corrosion evident	NaCl	Calcite	etches, micro- pitted, light corrosion	very heavily etched and micro pitted	etches	etches	etches, micro- pitted, micro corrosion	etches	etches	light crevice corrosion etches micro pitted	
517'4"-519'4"	change from light to dark	essentially no corrosion	slight corrosion on exterior surface of wires	---	---	etches and micro pitted	striated etches micro pitted	etches	striated micro crevice corrosion	etches micro-etched corrosion	etches	etches	micro pitted corrosion	
1004'7"-1008'7" (just above side rubber jacket)	dark	some evidence of slight crevice corrosion	new evidence of slight crevice corrosion	---	---	etches pitted	etches pitted corrosion	slight to moderate corrosion						
1004'7"-1008'7" (clean end)	dark, slight rust	some corrosion on outer wires	irregular corrosion on some wires	---	---	etches pitted	etches pitted corrosion	slight to moderate corrosion						
1004'7"-1008'7" (transition - under neoprene jacket)	heavily rusted, wire rope damp under neoprene jacket)	some irregular corrosion on wires	considerable evidence corrosion on exterior surfaces of wires	---	---	etches pitted corrosion	moderate to severe corrosion							
1008'7"-1010'7" (under neoprene jacket)	heavily rusted, wire rope damp	3 small outer wires tunnelled, some crevice corrosion	considerable crevice corrosion on some wires	---	---	etches, striated, crevice corrosion, pitted, heaved down	striated, pitted, heaved down severe crevice corrosion	etches, pitted, heaved down severe crevice corrosion	etches, pitted, heaved down severe crevice corrosion	etches, pitted, heaved down severe crevice corrosion	etches, pitted, heaved down severe crevice corrosion	etches, pitted, heaved down severe crevice corrosion	etches, pitted, heaved down severe crevice corrosion	moderate to severe corrosion
1008'9"-1090'9" (under neoprene jacket)	bright, H ₂ O present	essentially no evidence of corrosion	corrosion outer surfaces of wires	---	---	etches pitted delamination	etches and pitted							
1231'5"-1233'5" (9 1/2' above uppermost lower cable clamp, under neoprene jacket)	corroded	3 small outer wires tunnelled, exterior corrosion on small wires	some irregular corrosion	7Fe(OH) NaCl	Fe ₂ O ₃ (OH) NaCl	etches pitted delamination	etches, crevice corrosion, deeply heaved down striated							
1233'5"-1244'5" (wire under lower cable clamp)	corroded	irregular corrosion on some strands	irregular corrosion on some wires in some strands	---	---	severely pitted and crevice corrosion in clamped areas, other areas etched and pitted	severely pitted and crevice corrosion in clamped areas, other areas etched and pitted	severely pitted and crevice corrosion in clamped areas, other areas etched and pitted	severely pitted and crevice corrosion in clamped areas, other areas etched and pitted	severely pitted and crevice corrosion in clamped areas, other areas etched and pitted	severely pitted and crevice corrosion in clamped areas, other areas etched and pitted	severely pitted and crevice corrosion in clamped areas, other areas etched and pitted	severely pitted and crevice corrosion in clamped areas, other areas etched and pitted	severely pitted and crevice corrosion in clamped areas, other areas etched and pitted

* Spectrographic analysis gave very strong lines for Ca, Mg, Si and strong lines for Fe.
 * Spectrographic analysis gave strong lines for Cr, Ni, Cu, Mn, and Si and very strong lines for Fe.

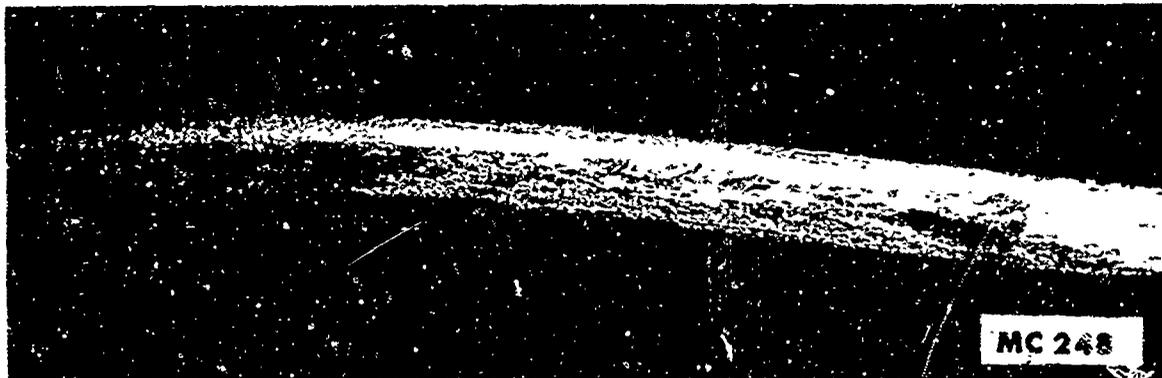
Table 2

Corrosion on 304 Stainless Steel Fittings Used On Nomad Buoy Moor
(34 months continuous service in seawater, lat 25--00N, long 90-00W)

Fittings and Locations	Observations
<u>Clamps</u>	
Upper	Mechanical crazing or alligatoring. In wire rope area clamp has pronounced imprint of wire rope.
Lower	Some crevice corrosion on crowns of threads. In wire rope area clamp has pronounced imprint of wire rope. Few micro pits in threads.
<u>Clamp Nuts</u>	
Upper Clamp	Essentially no crevice corrosion at crown of thread.
Lower Clamp	Some crevice corrosion at crown of threads.
<u>Tube Thimbles</u>	
Upper	Surface roughening inside and outside and local pitting in heat-affected zone. One section cracked at weld of doubler. May have been caused by undercutting or a cold weld.
Lower	Some shallow pitting on outside, and spotted areas of light corrosion on inside. Some pitting adjacent to weld.

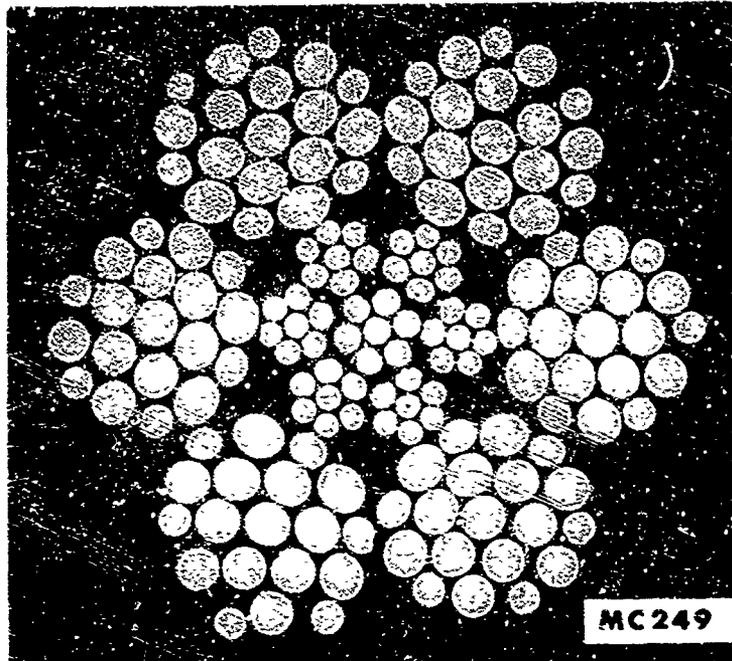


(a) Cross section (5X magnification)

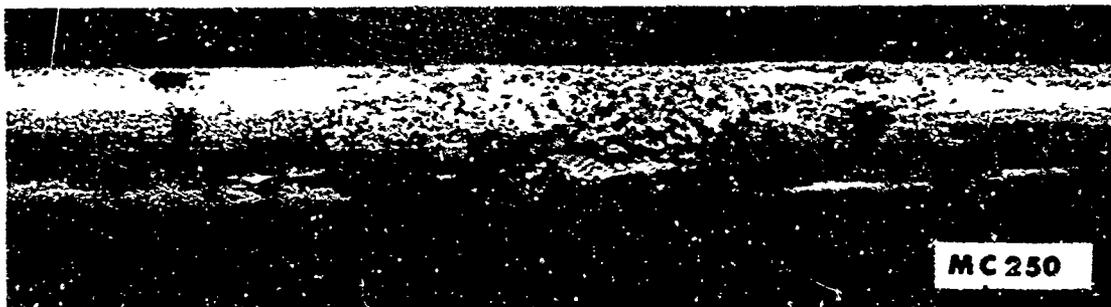


(b) IWRC, center strand, outer wire
(15X magnification)

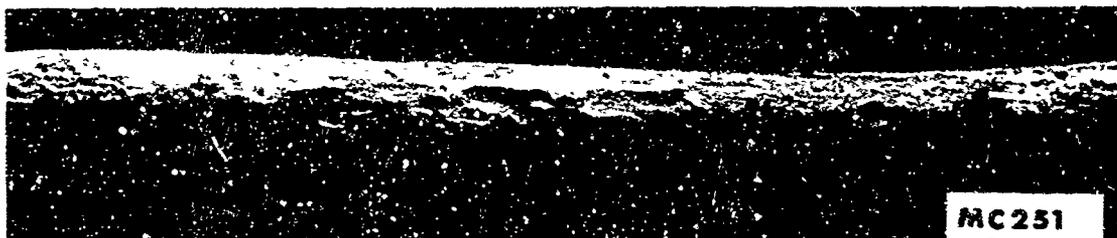
Fig. 1 - 304 stainless steel wire rope after 34-months continuous immersion as part of a Nomad buoy mooring system, showing the essential absence of corrosion at a distance of 11-13 ft from the top of the wire rope.



(a) Cross section (5X magnification)

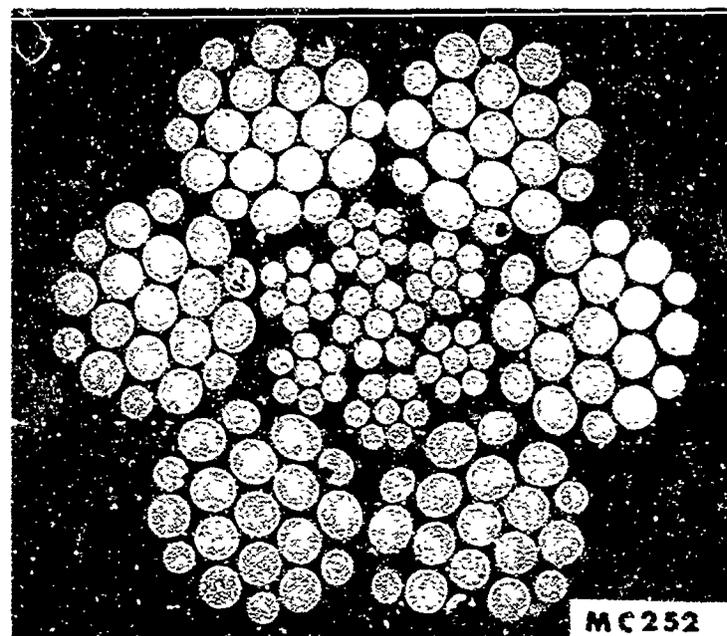


(b) Outer strand, inner wire
(15X magnification)

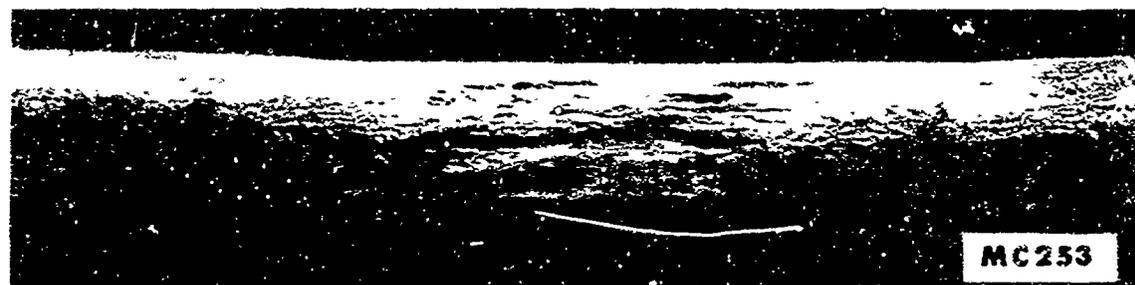


(c) IWRC, center strand, outer wire
(15X magnification)

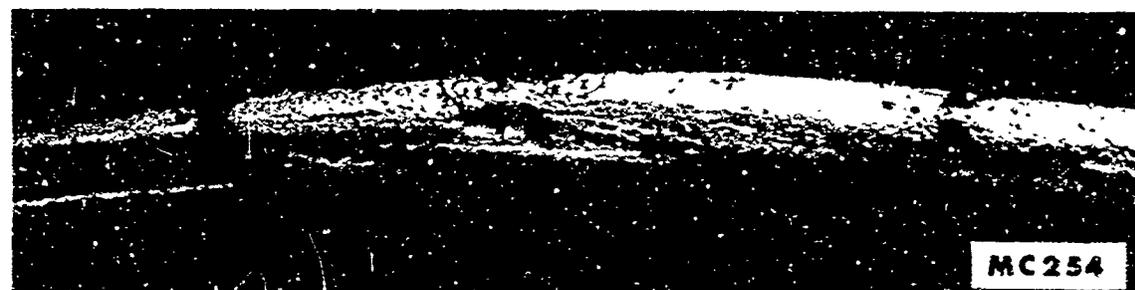
Fig. 2 - 304 stainless steel wire rope after 34-months continuous immersion as part of a Nomad buoy mooring system, showing the moderate-to-severe corrosion at a distance of 1006 ft-7 in. to 1008 ft-7 in. from the top of the wire rope (rusted end of transition - under neoprene jacket).



(a) Cross section (5X magnification)

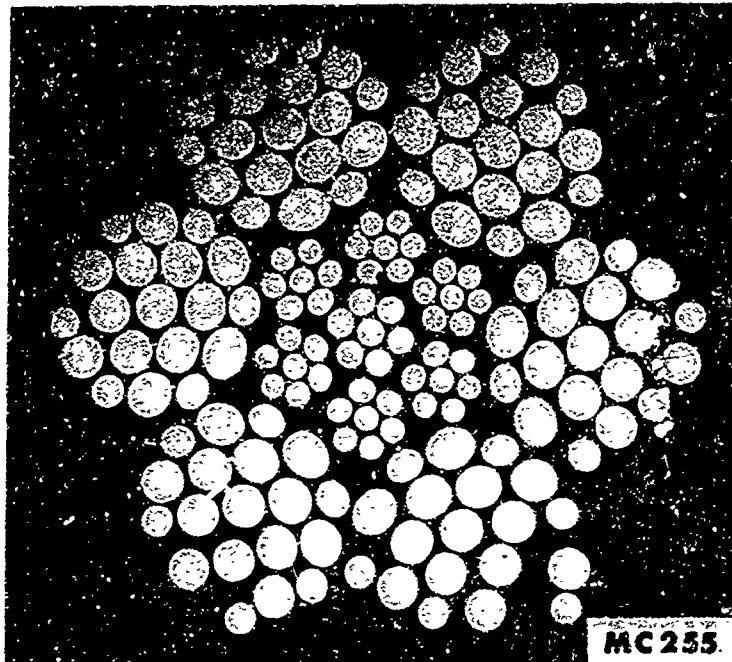


(b) Outer strand, inner wire
(15X magnification)

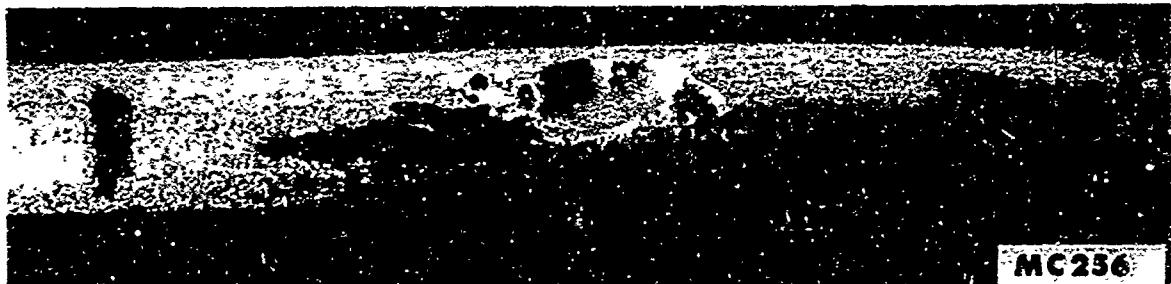


(c) IWRC, center strand, outer wire
(15X magnification)

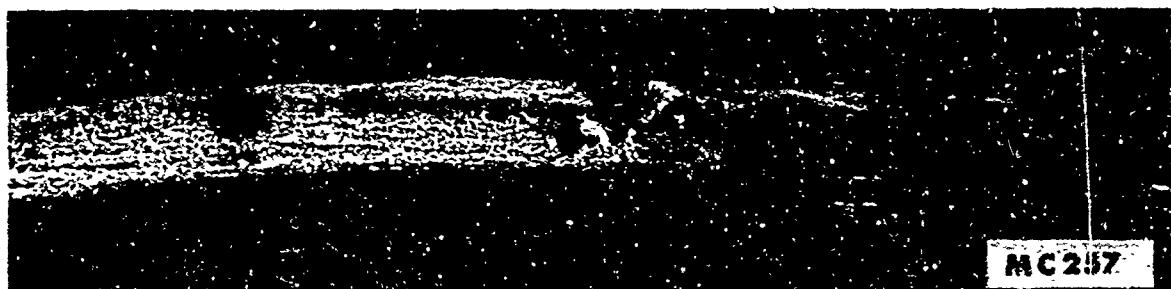
Fig. 3 - 304 stainless steel wire rope after 34-months continuous immersion as part of a Nomad buoy mooring system, showing (a) tunnelling and (b) and (c) severe corrosion at a distance of 1008 ft-7 in. to 1010 ft-7 in. from the top of the wire rope (under neoprene jacket).



(a) Cross section (5X magnification)

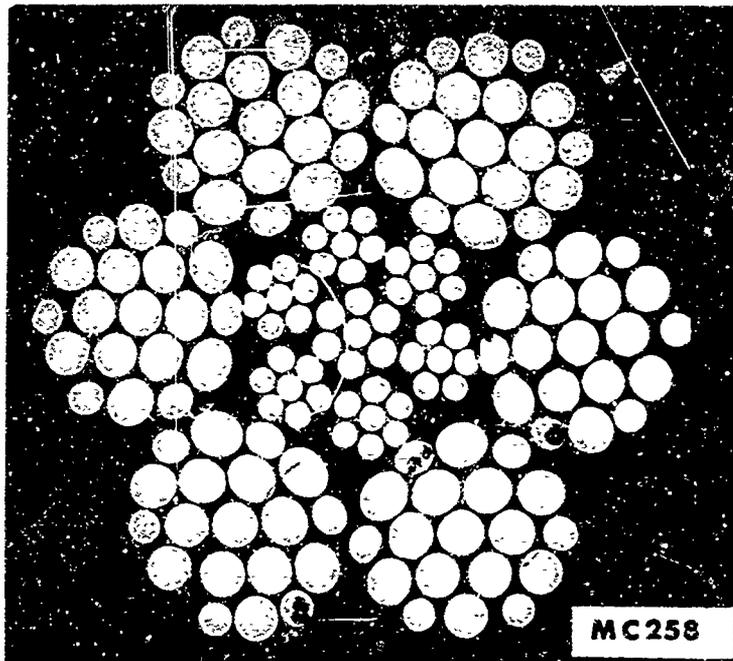


(b) Outer strand, large outer wire
(15X magnification)

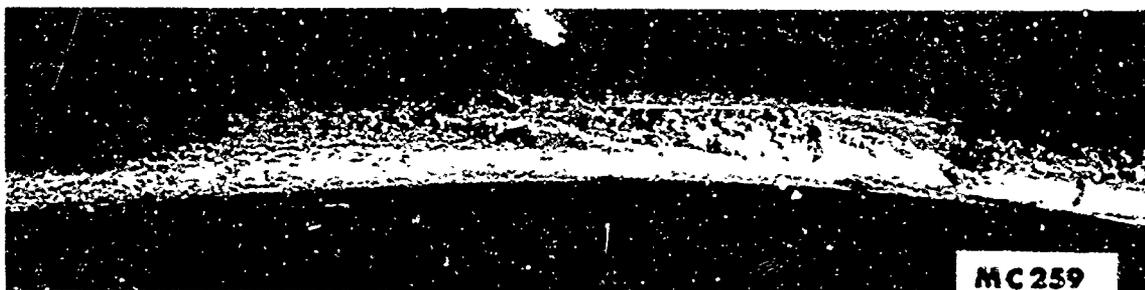


(c) IWRC, center strand, outer wire
(15X magnification)

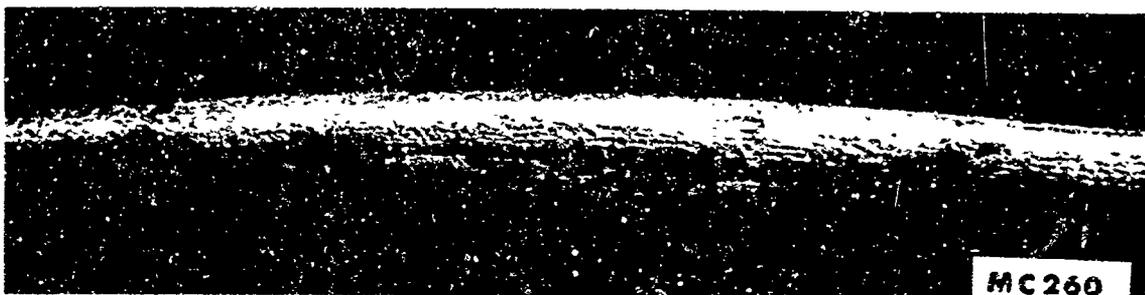
Fig. 4 - 304 stainless steel wire rope after 34-months continuous immersion as part of a Nomad buoy mooring system, showing (a) limited tunnelling, but (b) and (c) deep pitting on individual wires at a distance of 1088 ft-8 in. to 1090 ft-8 in. from the top of the wire rope (bright appearance under jacket).



(a) Cross section (5X magnification)



(b) Outer strand, outer small wire
(15X magnification)



(c) IWRC, center strand, outer wire
(15X magnification)

Fig. 5 - 304 stainless steel wire rope after 34-months continuous immersion as part of a Nomad buoy mooring system, showing (a) severe tunnelling, (b) pitting and crevice corrosion, and (c) cracked area of a wire at a distance of 1231 ft-5 in. to 1233 ft-5 in. from the top of the wire rope.

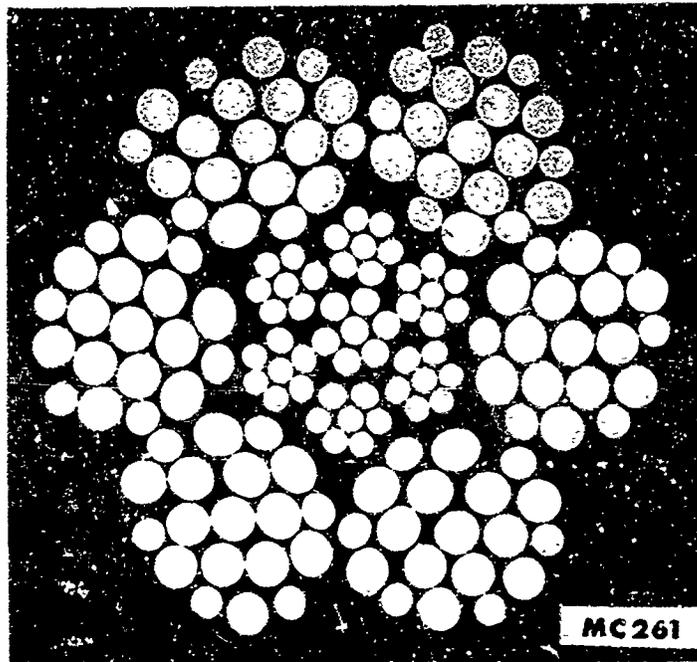


Fig. 6 - 304 stainless steel wire rope after 34-months continuous immersion as part of a Nomad buoy mooring system, showing the good condition of the wire rope under a cable clamp at the top of the wire rope (5X magnification).

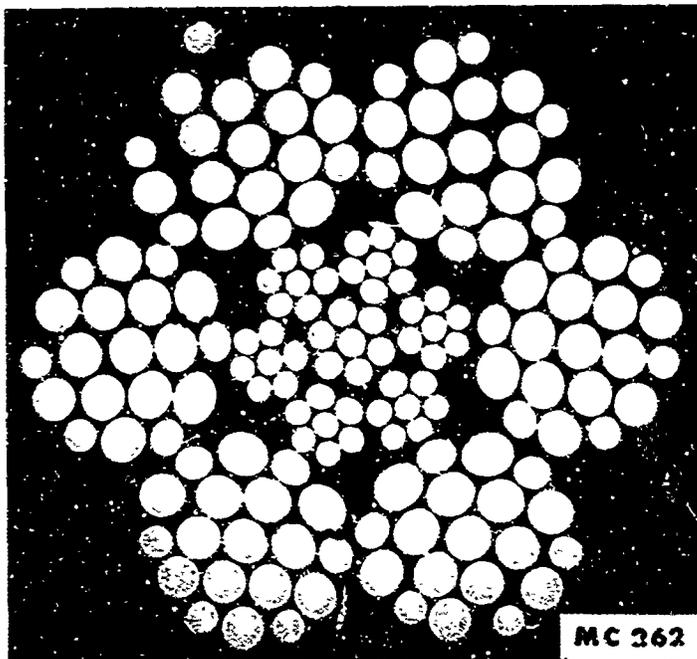


Fig. 7 - 304 stainless steel wire rope after 34-months continuous immersion as part of a Nomad buoy mooring system, showing corrosion at periphery of some wires under a cable clamp near the bottom of the wire rope (clamp and wire rope shielded with tape) (5 magnification).

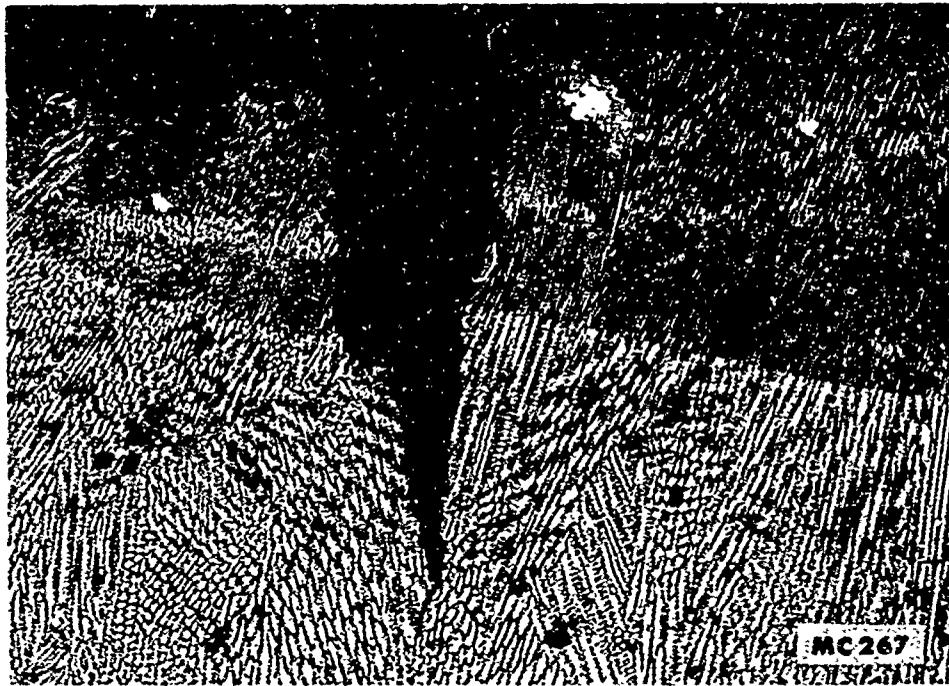


Fig. 8 - 304 stainless steel wire rope after 34-months continuous immersion as part of a Nomad buoy mooring system, showing severe pitting and crevice corrosion under a cable clamp near the bottom of the wire rope (clamp and wire rope were shielded with tape) (15X magnification).

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(a) Unetched (100X magnification)



(b) Electrolytic etch - 10% oxalic acid
(100X magnification)

Fig. 9 - Section of 304 stainless steel wire rope tube thimble showing crack which may have been caused by a cold weld or by undercutting during welding.

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13. ABSTRACT <p>Samples from a 1250-ft length of 304 stainless steel wire rope and associated stainless steel tube thimbles and stainless steel cable clamps were studied to determine the extent of corrosion after 34-months continuous immersion in the Gulf of Mexico. This 3/4-in.-diam wire rope (6 x 19 Warrington - IWRC 7 x 7) was used in the upper portion of a Nomad buoy mooring system. The performance of this particular buoy design is important because of its possible influence on the national buoy program.</p> <p>The absence of any significant corrosion on the top 1000 ft of this stainless steel wire rope was attributed to the beneficial effects of the retained lubricant, to the cathodic protection from a steel anode located just above the wire rope, and to probable inadvertent cathodic protection from the 6061-T6 aluminum surface buoy.</p> <p>The lower 250 ft of the wire rope was jacketed with neoprene to prevent abrasion of the synthetic rope used for the lower section of the mooring system. The distance from the anode and the electrical shielding effect of the jacket prevented effective cathodic protection of this section of the rope, and relatively severe corrosion was observed.</p> <p>Experience gained in this stainless steel wire rope analysis and other wire rope corrosion analyses currently being conducted indicates that one cannot determine the extent of corrosion of wire ropes</p> <p>(contd)</p>		

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by an inspection of only the exposed external surfaces. This is especially true when a material such as the common grades of stainless steel is used because the corrosion of such material occurs locally by tunnelling or crevice corrosion or pitting and, therefore, may not be evident externally. For certain critical applications, i.e., where the system is not extremely over-designed, it may be necessary to replace the wire rope at the first sign of rope deterioration as evidenced by rusting or whiskering.