

This document was produced
by scanning the original publication.

Ce document est le produit d'une
numérisation par balayage
de la publication originale.

P. M. D. File
INDUSTRIAL CONFIDENTIAL

DECLASSIFIED

CANADA

DATE JUN 15 1979

AUTHORIZED BY

W. H. Erickson

DEPARTMENT OF MINES AND TECHNICAL SURVEYS

OTTAWA

IR 62-112

MINES BRANCH INVESTIGATION REPORT IR 62-112

EXAMINATION OF ARSENIC-INHIBITED ADMIRALTY BRASS CONDENSER TUBES

by

J. O. EDWARDS

PHYSICAL METALLURGY DIVISION

COPY NO. 9

CANMET LIBRARY

DECEMBER 13, 1962

Declassified
Déclassifié

~~Industrial Confidential~~

Mines Branch Investigation Report IR 62-112

EXAMINATION OF ARSENIC-INHIBITED ADMIRALTY
BRASS CONDENSER TUBES

by

J. O. Edwards★

- - - - -

SUMMARY OF RESULTS

A sample of tube from the propane condenser of an oil refinery was shown to have failed by stress corrosion cracking. Considerable general corrosion was also present, indicating aggressive conditions on the hydrocarbon gas side of the tubes.

Recommendations were made with regard to selection of tube materials and operation of the condenser to limit corrosive attack and, hence, improve tube life.

★ Head, Non-Ferrous Metals Section, Physical Metallurgy Division, Mines Branch, Department of Mines and Technical Surveys, Ottawa, Canada.

INTRODUCTION

On October 17, 1962, Mr. A. G. Stewart, Refinery Manager, Imperial Oil Limited, Regina Refinery, wrote to the Information Services Division of the Saskatchewan Research Council outlining the failure of arsenic-inhibited admiralty brass condenser tubes in the Propane Condenser 2-E-4 of their Butane Recovery System. It was stated that the operating conditions of the condenser were as follows:

A. Hydrocarbon Side (Outside surface of tubes)

Operating Pressure PSIG 200

Operating temperature °F 105 In. 95 Out.

Composition of hydrocarbon

<u>Component</u>	<u>Mol. %</u>
H ₂ S	1.0
Methane	2.9
Ethylene	2.8
Ethane	19.4
Propylene	4.8
Propane	68.9
Iso-Butane	0.2

B. Water Side (Inside surface of tubes)

Operating Pressure psig 25

Operating Temperature °F 65 In.
85 Out.

pH of water 6.5

Help was requested to determine the corrosion mechanism, and also to analyse the tube for arsenic and zinc since dezincification was suspected.

In a reply of November 6, 1962, (Ref. No. 7825) Mr. Scharf of the Saskatchewan Research Council gave the following results of comparative X-ray fluorescence analysis:

	Zn etch %	As	Fe	Sn
New Brass (assumed composition)	27.31	.06	.06	1.0
Corroded Brass ★ (uncorroded interior)	27.31	.08	.06	1.2
(corroded side)	24 approx. only			
Scale	All elements present			

★ These values are strictly relative to assumed composition of new brass

The enquiry was then turned over to the Technical Information Service of the National Research Council, Ottawa, who in turn passed it on to this Division with a covering letter on November 21, 1962 (F. G. Halang, File No. 53678).

On November 26, further information was requested concerning the operating conditions at the refinery since initial examination revealed excessive corrosion on the outside (hydrocarbon side), which would not be expected if the conditions were as originally stated. In a reply dated December 10, it was admitted that water was occasionally present in the system.

VISUAL EXAMINATION

The surface of the tube had been cleaned, but in some areas, patches of a black film resembling graphite were still present on the outside of the tube. A thinner black deposit was also visible on the inside, and overall pitting of the inside surface of the tube was apparent. This is shown in Figure 1.

The most remarkable feature of the tube was the extensive cracking and veining on the outside as shown in Figures 2 and 3. This ranged in character from a straight crack on the longitudinal axis which completely perforated the tube to a widely branching crack which also perforated the tube. There were a large number of smaller cracks - particularly the widely branched ones - which had not completely perforated the wall.

The nominal wall thickness of the tube was 0.065 in., and micrometer measurements showed that this had been reduced to an average of 0.061 in.

HARDNESS TESTS

Hardness tests were carried out on cross-sections of the corroded tube and a section from a new 3/4 in. tube of greater wall thickness (12 BWG as compared to 16 BWG of the failed tube), which was supplied for comparison purposes. The results are given below:

	Rockwell Superficial Hardness	
	15T Scale	30T Scale (converted)
Corroded Tube	75	46
New Heavy Gauge Tube	80	56

No hardness is specified for condenser tube material but for comparison it may be noted that the specified hardness for fully annealed 70/30 brass plate of the same grain size (0.025 mm) is 27-42 R30T.

METALLOGRAPHIC EXAMINATION

Sections were taken from the tube in areas containing branching cracks, and straight cracks orientated in the longitudinal axis. The sections were mounted and polished, and examined in both the unetched and etched conditions.

The cracks all originated in the outside surface of the tube and, in general, were blunt ended and filled with corrosion product. Figure 4 represents two typical cracks, although the majority of the cracks observed were relatively straight, as shown by the crack on the right. The cracks seemed to have the same general structure whether they appeared branched or straight on the surface, but this cannot be stated definitely as the nature of the crack was masked by the corrosion product.

Occasional cracks were observed that had not been heavily corroded, presumably because they were of fairly recent origin. Figure 5 is representative of such a crack and Figure 6 shows an enlarged view of the tip of the crack in the etched condition from which it is apparent that the cracks are transcrystalline as well as intercrystalline.

CHEMICAL ANALYSIS

In view of the analysis carried out by the Saskatchewan Research Council which indicated that the material corresponded to arsenic-inhibited admiralty brass, no further analyses were carried out at the Mines Branch. However, spectrographic and X-ray fluorescence analysis of the corrosion scale sample (which presumably came from the outside of the tube, although this was not stated) indicated that the main constituents were copper, zinc and iron. Diffraction patterns could not be positively identified but were suggestive of complex copper-iron sulphides, and part of the scale was strongly magnetic, indicative of iron oxide.

DISCUSSION

The failure of the tube must be attributed to unusually aggressive conditions in the propane condenser (assuming similar units are giving satisfactory service elsewhere), to faulty material, or to a combination of both.

With regard to the material, the chemical composition appears satisfactory and no defects could be observed in the microstructure. The longitudinal cracking, which is obviously associated with fabricating techniques, suggests that there may have been seams or stringers of inclusions in the pipe. Although these may have been eaten out by subsequent corrosion, there is no indication of this in the microstructure, and it is suggested that this is a special case of the overall cracking found in the tube. The appearance of the cracks that are not masked by corrosion product is typical of stress corrosion cracking in arsenic-inhibited brass. (Corrosion fatigue cracks would have a similar appearance in the microstructure, but on the

macro-scale would be oriented relative to the direction of applied stress, whereas the branching cracks in the failed tube have a random orientation.) This suggests that the tubes may not have received a complete stress relief anneal, or that they had been stressed again during fabrication or operation of the propane condenser. The hardness tests suggest that the tubes may not be fully annealed, but hardness conversions for comparison are always doubtful, and it should be noted that the failed tube is in any case softer than the new, unused tube.

With regard to the operating conditions of the condenser, it appears from the letter of December 10 from the Regina Refinery that liquid water is occasionally drained from the reflux drum attached to the condenser, and from the flow sheet given, it appears that the gas might be relatively high in water vapour at the time it reaches the condenser tubes, as water is drained each shift from the feed drum. Since the water in the condenser tubes is at 65-85°F, and the minimum feed temperature shown on the flow sheet is 100°F, it seems likely that dew point might be reached on the surface of the tubes under unfavourable conditions. Also, steam is used to purge the system on shut down and start up which occurs about three times per year. Thus, despite the statement that "analysis of the overhead gases (in the letter of October 17) did not show water vapour present as this is not a normal occurrence", it is apparent that, at least on occasion, water vapour and even water has been present in substantial quantities. Thus, severe corrosion in the presence of hydrogen sulphide might be expected and, under certain conditions, stress corrosion might also occur, leading to catastrophic failure of the tubes such as was observed.

As the cause of the failure may lie in either the metal or the operating conditions, the remedy must also be sought in both fields.

Although no evidence could be obtained that the metal was faulty, it is possible that defects did exist, and that the tubes were susceptible to stress corrosion in that they may not have been annealed, or had been unduly stressed during fabrication or in operation. This could perhaps be determined by a more complete examination of this and other tubes in the condenser. It is also possible that other alloys may give better service, the lower zinc alloys (such as 85/15 brass) are less susceptible to stress corrosion, but suffer more rapid overall corrosion in moist hydrogen sulphide. A satisfactory compromise may also be reached by the substitution of cupro-nickel or other materials for the brass.

No detailed comments can be made about altering refinery conditions, but it is obviously highly desirable to operate as dry a system as possible, and to ensure that no traces of ammonia and mercury (mercury vapour escapes readily from mercury manometers) are present in the gases since these agents actively promote stress corrosion cracking. Although it is not considered that the thrice-yearly steaming was a major factor, the system should be dried out as quickly as possible after such operations.

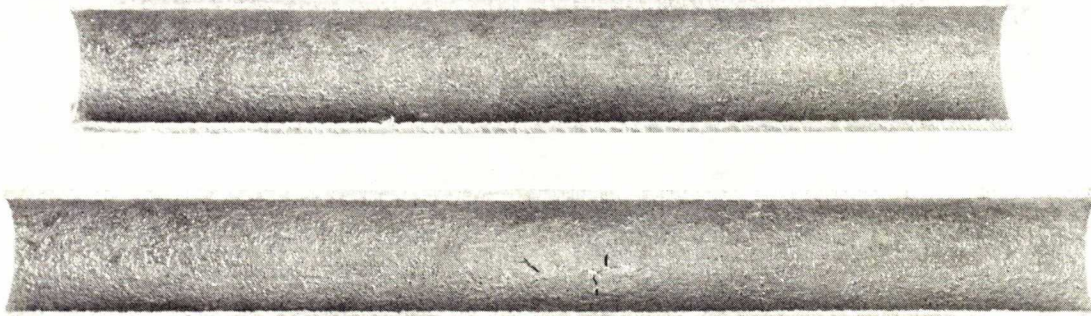


Figure 1. Inside surfaces of failed tube. Note pitting and perforation by branching crack in lower section. (approx. full size)

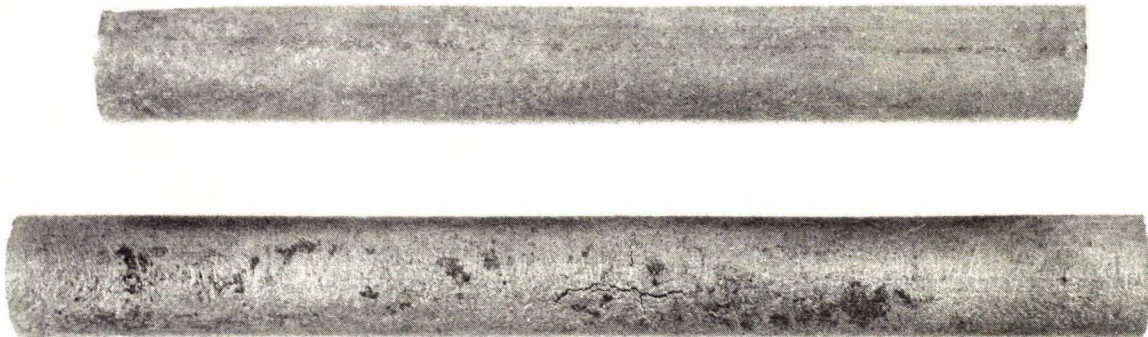


Figure 2. Outside surfaces of failed tube showing overall branching cracks, particularly in lower section. (approx. full size)

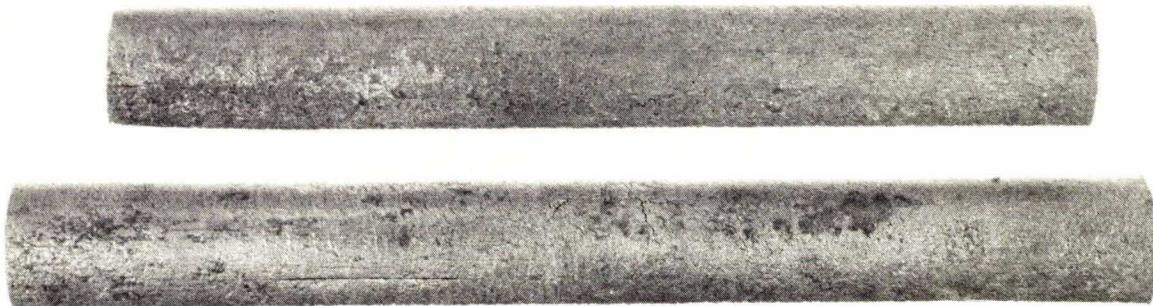


Figure 3. As in Figure 2 showing both branching cracks and straight cracks. (approx. full size)



Figure 4. Pitting and cracks full of corrosion product. Outside surface of tube. X150 Unetched.

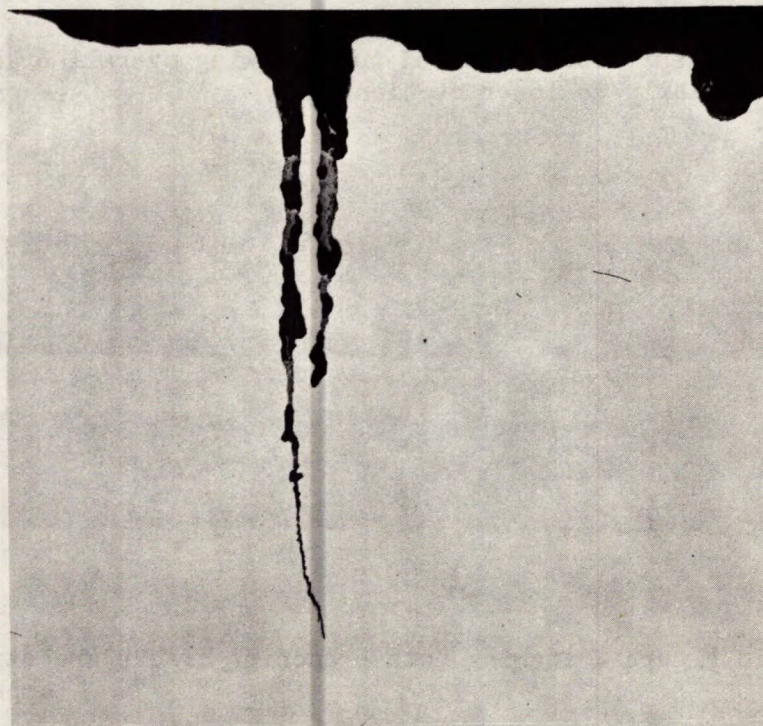


Figure 5. Double crack, one of which shows well-defined tip, probably of recent origin. X75 Unetched.

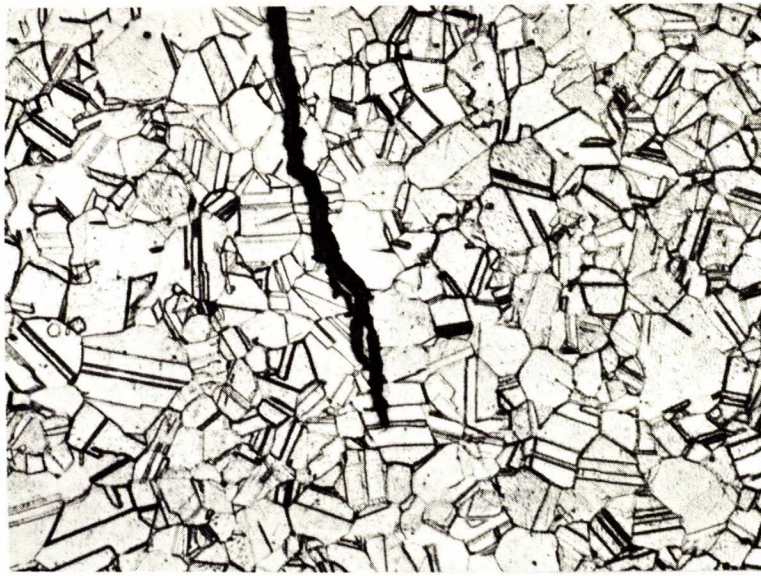


Figure 6. Tip of crack showing both transcrystalline and intercrystalline nature of crack propagation. X300