Corrosion of Alloys in Tall Oil Distillation Service

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Abstract

Plant corrosion tests of various metals and alloys in tall oil distillation streams present the effect of alloy composition on corrosion rate. Stream temperature, alloy composition and stream composition are correlated so as to provide a useful guide to material selection for tall oil distillation plants. Alloys exposed to corrosion test were iron or nickel base with chromium plus varying amounts of molybdenum. Molybdenum is the most important alloy addition in reducing the rate of corrosion attack, with corrosion attack at a very low rate, <.1 mil per year, at the 6% molybdenum level in the most aggressive stream tested, i.e., 85% fatty acids at 518 F. The presence of chromium does not appear to be essential to obtaining good corrosion resistance to the more corrosive conditions. Corrosion rates increase with increasing temperature. The streams classed as high in fatty acids are much more corrosive than those which are classed as high in rosin acids. Vapor phase streams are more corrosive than liquid phase streams. Corrosion attack is normally from pitting. Most of the more corrosive conditions can be handled with an alloy containing 3% to 4% molybdenum (AISI Type 317), but some process conditions require higher molybdenum contents in order to obtain acceptable corrosion rates. Less corrosive streams can be handled with an alloy containing less than 3% molybdenum (AISI Type 316).

Corrosion of the alloys of construction used in tall oil distillation plants is a problem which our earlier work dealt with on a fairly comprehensive basis based on empirical test results in a number of plants (1,2). The purpose of this work was to fill in some of the gaps which exist in the present data, to study some of the corrosion mechanisms encountered and to try and establish broader parameters for alloy selection than exist at the present time.

All data presented here was obtained from in plant exposures using corrosion test rods of the type described previously. This continuing work has been made possible through the cooperation of distillation plant operators who were willing to release enough information on exposure conditions to provide meaningful results, yet not reveal confidential process information.

The earlier works clearly pointed out the much greater corrosion potential of the streams which are high in fatty acid content. Vapor phase exposures were in general more corrosive than liquid phase exposures. Increasing temperature appears to produce higher corrosion rates but the correlation was found to be poor.

These more recent tests were made in the hopes of answering some of the questions left by the earlier work and materials exposed were selected with this thought in mind. The basic alloy for comparison performance is the CF 8M alloy (2.4% Mo), the cast alloy of composition similar to wrought type 316.

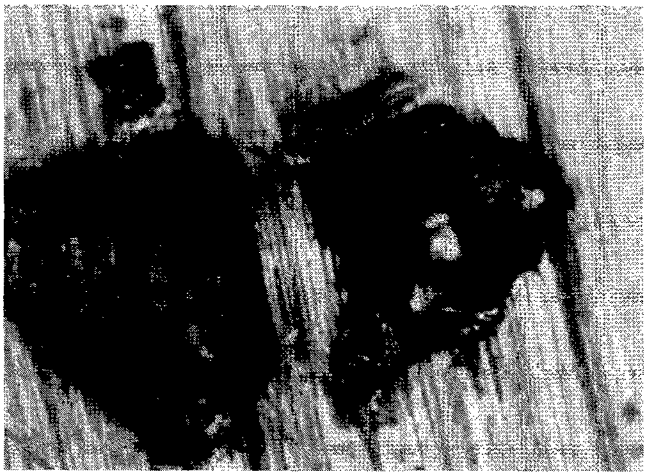

FIG. 1. Two pits in surface of 2.4% Mo, CF 8M sample 200x (Table V), which are typical of pitting produced in tall oil distillation streams.

Test exposures covered here all fall into the category of being exposed to process streams high in fatty acids. Corrosion rates are reported as penetration in mils per year computed from the weight loss. Additional observations concerning the corrosion attack and specimen appearance are given in the data tables.

Tables I and IV list the composition of all the alloys exposed with appropriate notation as to whether the analysis was nominal or actual. Samples made from cast alloys are identified by the use of cast alloy designations, samples made from wrought alloys are identified by the use of wrought material designations.

Table II gives the results of an exposure in 85% fatty acids, 15% rosin acids agitated by sparge steam at 270 C (518 F) for an exposure time of 720 hr, in the liquid phase. The only samples not severely attacked were the CW 12M (Cast Hastelloy C) and the N 12M (Cast Hastelloy B). We see again the decreasing corrosion rate of the austenitic nickel-chromium stainless steels with increasing molybdenum content: 180 mils/year at 2.4% molybdenum content decreasing to 40 mils/year at 3.2% molybdenum.

Table III gives the results of an exposure in 85% fatty acids, 15% rosin acids agitated by sparge steam at a temperature from 265 C to 287 C (509 F to 549 F) for an exposure time of 1752 hr, in the liquid phase. The Hastelloy B and C were almost totally resistant to these conditions paralleling the results of the exposure cited in Table II. The effect of molybdenum on the corrosion

TABLE I
Nominal Composition of Samples Exposed, Tables II and V, %

Alloy	C	Cr	Ni	Mo	Mn	Si	Cu	Other
CF 8M (2.4% Mo)	.06	19.50	10.50	2.4[a]	.75	.80	......	....
CF 8M (2.75% Mo)	.06	19.50	10.50	2.75[a]	.75	.80	......	....
CG 8M	.06	19.50	11.00	3.2[a]	.75	.80	......	....
317	.06	19.00	13.00	3.2	1.50	.50	......	....
CN 7M (A 20)	.05	20.00	28.00	2.5	1.00	.75	3.5	....
CY 40 (Cast inconel)	.12	13.5	77.5	....	.80	1.00	......	Fe bal.
M35 (Cast monel)	.12	....	67.00	....	.75	1.25	30.0	Fe bal.
N 12M (Cast Hast. B)	.06	....	Bal.	28.0	.85	1.00	......	Fe 5.0, V 0.4
CW 12M (Cast Hast. C)	.10	16.50	Bal.	17.0	.75	.90	......	Fe 5.5 W 4.25
2S aluminum								Commercially pure Al
RC 70 titanium								Commercially pure Ti

[a] Actual analysis.

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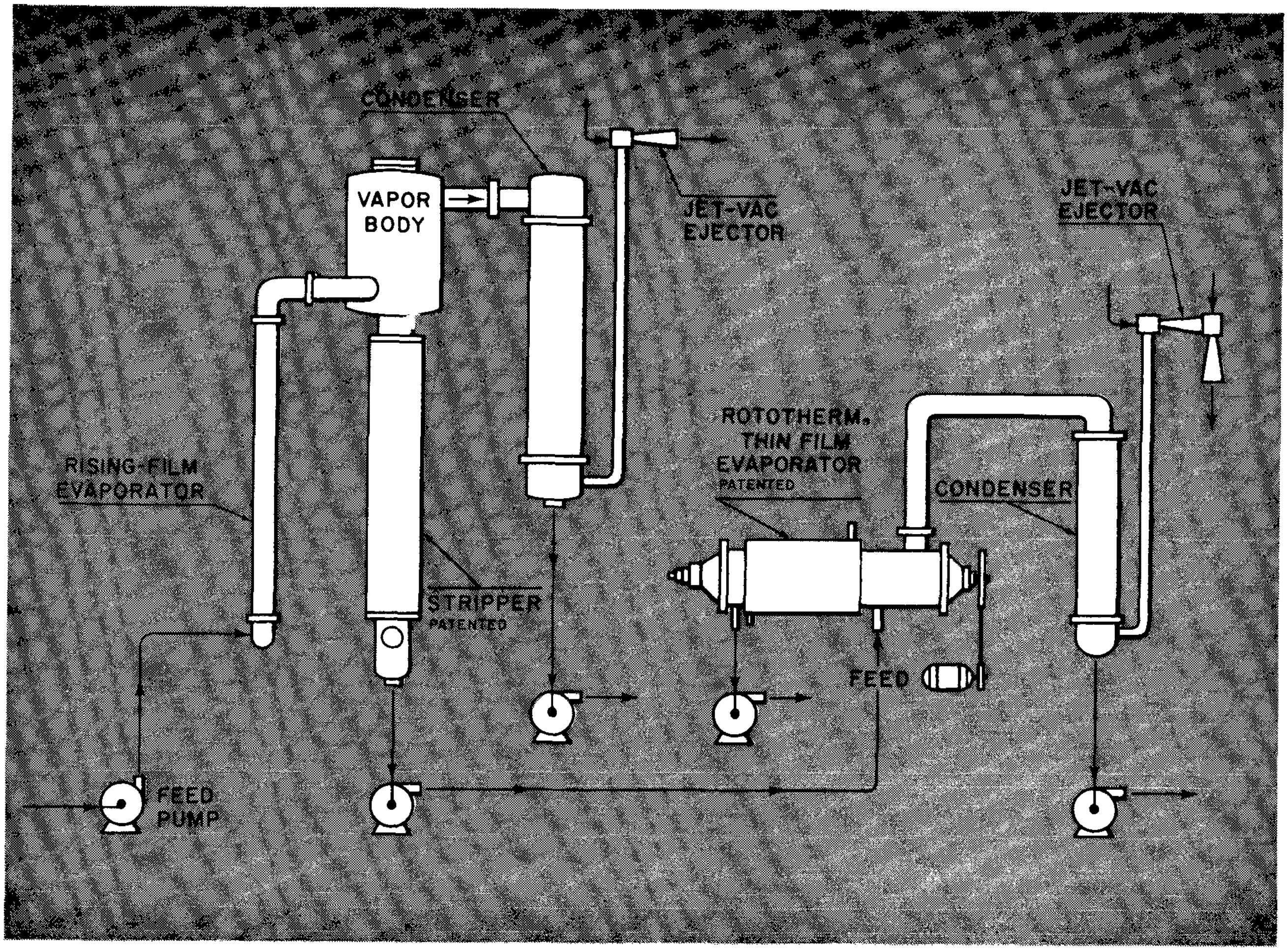

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TABLE II
Six Inches Above Tube Sheet in Heat Exchanger[a]

Alloy	Penetration Mils per Year	Remarks
CF 8M (316 Cast) 2.4% Mo	180.6	Very heavy, even attack
CF 8M (316 Cast) 2.75% Mo	123.9	Very heavy, even attack
CG 8M (317 Cast)	40.6	Heavy rough attack
Type 317	36.4	Moderate, comparatively smooth attack
N 12M (Cast Hast. B)	....	Sample damaged in cleaning, attack estimated to be same as CW 12M
CW 12M (Cast Hast. C)	0.2	Very light etch

[a] Solution: tall oil, 85% fatty acids, 15% rosin acids, agitated by sparge steam, 270C (518F), liquid phase, 720 hr.

TABLE IV
Actual Composition of Samples Exposed, Table III, %

Alloy	Cr	Ni	Mo	Cu	Fe
Hastelloy B	0.3	65.8	27.65	....	4.5
Hastelloy C	14.8	56.4	16.37	....	5.5
Hastelloy F	21.8	45.9	6.56	....	20.6
CN 7M (Aloyco 20)[a]	20.0	28.5	2.5	3.5	......
Carpenter 20	20.3	27.4	2.23	3.36	......
Type 316	17.6	12.5	2.19	....	......
Type 317	18.7	13.6	3.30	....	......
Nionel 825	20.6	41.4	3.00	1.72	......
Monel 400	......	67.4	....	30.0	......
Inconel 600	16.1	76.3	....	....	7.1
Incoloy 800	21.4	30.2	....	....	47.2
Incoloy 804	30.5	41.5	....	....	25.4
Incoloy 901	13.2	44.0	5.75	....	32.9

[a] Nominal composition.

resistance of the nickel-chromium alloys is much the same as we have seen before. The results of this test are particularly noteworthy because samples with molybdenum contents of 5.75% and 6.56% were included, and corrosion rates at these molybdenum levels were negligible (0.1 mil/year with no reported pitting).

Table V gives the results of one exposure in distillation streams which varied in composition as indicated. Both streams handled would be classified as high in fatty acids and the test was in the vapor phase. Attack on the molybdenum bearing stainless steel was negligible and pitting was found only on the 2.4% molybdenum content nickel-chromium stainless steel. The pitting was minor, only a total of six pits, all very small and less than 0.001 in. deep. The inconel speciman was severely corroded indicating the unsuitablity of this alloy for such service. Stainless steels with molybdenum content above 2.4% should be selected for such service to fully suppress the pitting tendency of the distillation stream.

Corrosion Mechanism

As a part of this work detailed microscopic examinations were made on many samples in an effort to determine the probable corrosion mechanism. Examinations were made directly on the corroded specimen surface after cleaning and also on cross sections cut from corroded specimens.

The corrosion data tables in some cases indicate pitting attack and approximate depth of pits. In other cases the data tables refer to uniform corrosion attack or uneven attack of varying degrees of intensity. Pitting is usually determined by macro examination and is evidenced by localized perforation or penetration leaving the adjacent metal unattacked. Pits can be examined microscopically and if they are clean it is possible to focus on the bottom of the pit as well as the original surface permitting an approximate measurement of pit depth. Pit occurrence may be widely scattered or may occur with many pits per unit of area and pits may overlap giving the appearance of overall corrosion. Pit depth may be shallow or deep depending upon the alloy and the exposure conditions.

The samples of molybdenum bearing stainless steel from Table V, CF 8M (2.4% Mo), CF 8M (2.7% Mo) and CG 8M (3.2% Mo), were carefully examined on the microscope to determine if any pitting not visible to the naked eye had occurred or if any other visible corrosion had occurred.

The CF 8M sample (2.4% Mo) was found to contain only those pits which had been seen on macro examination, very small, shallow pits widely scattered over the specimen surface (a total of six pits on the entire specimen). The pits were found to be round bottom, somewhat irregular in profile and shallow (less than 0.001 in. deep). Figure 1 shows two pits in this specimen which are very close together that are typical of the other pits on this specimen. No corrosion other than the pits was found on this specimen.

The CF 8M (2.7% Mo) and CG 8M (3.2% Mo) samples from the exposure of Table V were found to be free of pits when examined microscopically and no corrosion of any type was found on these specimens. No pitting was found on any of the other specimens from this exposure. The Inconel specimen was too severely corroded to permit determination of the corrosion mechanism.

The molybdenum bearing stainless steel specimens from the exposure of Table II were all so severely corroded that it did not appear possible to determine the corrosion mechanism by microscopic examination. A corrosion transition zone has been noted on many specimens next to the area which was protected by the mounting washers, and that this transition zone appeared to have been attacked by pitting corrosion. Careful microscopic examination of this transition zone showed the corrosion attack to be the same type as illustrated in Figure 1, though much more severe with only very little unattacked metal between the pit sites which were often interconnected multiple pits. Examination of the corroded surface away from the transition zone shows complete attack of the original specimen surface, but leaving a roughened surface with the appearance of pits which have linked together producing a surface that might on cursory examination appear to have been the result of overall corrosion. Based on the results of this examination, it is concluded that pitting is the predominant if not the only type of corrosion mechanism involved on these samples in this exposure.

(Continued on page 172A)

TABLE III
Head of Tall Oil Heat Exchanger[a]

Alloy	Penetration, mils/year	Remarks
Hastelloy B	0.2–0.5	
Hastelloy C	<0.1	
Hastelloy F	0.1	
Incoloy 901	0.1	
Nionel 825	24.0	Spreading pits
Monel 400	36.0	
Type 317	39.0	Spreading pits
CN 7M (Aloyco 20)	41.0	
Inconel 600	63.0	Corrosion more rapid around spacer
Type 316	70.0	Spreading pits
Carpenter 20	76.0	
Incoloy 800	84.0	
Incoloy 804	90.0	Nearly destroyed

[a] Solution: tall oil, 85% fatty acids, 15% rosin acids agitated by sparge steam, 265–287C (509–549F) liquid phase, 1752 hr.

TABLE V
Fractioning Tower, Reboiler Vapor Nozzle[a]

Alloy	Penetration, mils/year	Remarks
CF 8M (Cast 316) 2.4% Mo	0.0	Bright and clean, few very widely scattered small pits
CF 8M (Cast 316) 2.7% Mo	0.0	Bright and clean
CG 8M (Cast 317)	0.0	Bright and clean
Nionel 825	0.0	Bright and clean
CW 12M (Cast Hast. C)	0.0	Bright and clean
RC 70 Titanium	0.0	Bright and clean
2S Aluminum	0.1	Light etch
CY 40 (Cast inconel)	15.9	Heavy overall attack

[a] Solution: (A) 82% linoleic-oleic acids, 5.5% rosin acids, 12.5% fatty acids above C-18, 888 hr; (B) 50% linoleic-oleic acids, 20% rosin acids 30% fatty acids above C-18, 3336 hr.
Vapor and liquid phase plus steam, ratio: Steam-vapor-liquid (5.7–6.0:1.0:0.01), 482–500F.