Corrosion of Alloys by Crude Fatty Acids at High Temperatures

by

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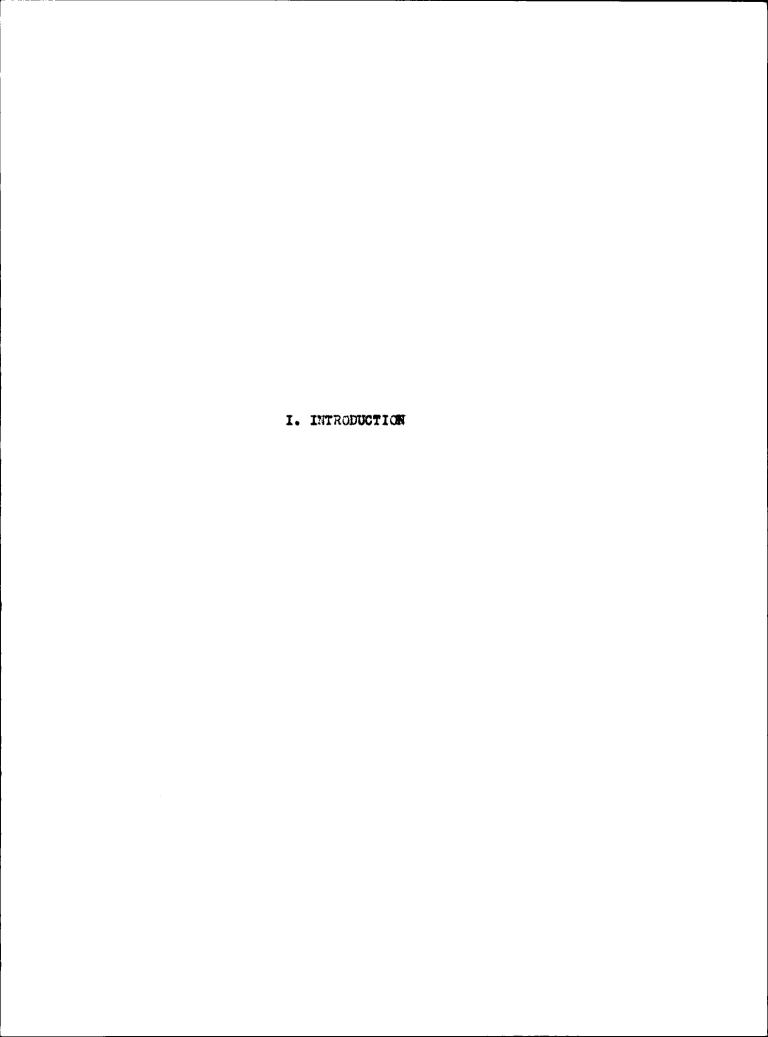
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I. INTRODUCTION

The factor of corrosion of materials of construction is one of the most important to be considered in the design of chemical plant equipment, for the majority of the chemicals used in processing equipment are of corrosive nature. Since the elementary metals are either too corrosive, expensive, or haven't enough strength, many alloys have been developed to overcome these difficulties. The corrosion rates of alloys have been studied in many corroding media, both in the laboratory and in the plant.

During the manufacture of kraft paper pulp from wood, the original fats and resins present in the wood are saponified by the caustic in the digesters into soluble scaps. These scaps pass out with the waste liquor into the concentrators where the digesting chemicals are removed. During this concentration process, these scaps, called sodium resinates, separate out and are removed. The mixture of scaps is treated with mineral acid to liberate the corresponding fatty acids which are called, in this country, crude fatty acids or crude tallol.

When these acids are heated to the distillation temperature, they cause considerable corrosion of the materials of construction and the replacement of equipment is necessary. For example (27), one-fourth inch copper tubes had to be replaced every three months in one plant. A great deal of work has been done in recent years to overcome this difficulty, but no final solution to the problem has been found although several alloys have been developed which are much better than those previously used for

equipment fabrication.

The distillation of the crude fatty acids is carried out in pipe stills under high vacuum. After each pass of the material through a section of the still, baffle plates remove some of the unvolatilised acids, and in this way a separation of the crudes is accomplished. Due to the mode of operation, there is a high velocity of vapors and liquids through the still which act to scour off any films which are formed on the tubes. It was for this reason that copper tubes corroded so rapidly, for as soon as a film was formed on the walls of the copper tubes, it was wiped away exposing fresh surface for attack.

The object of this thesis was to study the effect of varying compositions of iron, nickel, copper, and aluminum alloys on their corrodibility by crude tallol at three hundred degrees centigrade, and if possible to find a suitable material for the construction of tallol distillation equipment. For this purpose eighty-five commercial alloys were selected with wide ranges of composition whereby the effect of various alloying elements on the corrosion rate could be obtained.

II. REVIEW OF LITERATURE

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materials has been determined by a study of the findings of Hubscher (12), Dittmer (7), and de Keghel (5). To summarise their findings, the tallol contains approximately 50 per cent fatty acids, 40 per cent rosin acids, and 10 per cent unsaponifiable sterols and pitch. The fatty acids are composed principally of cleic, linoleic, and linolenic acids with small amounts of related acids, while the rosin acid is principally abietic acid.

Production in the United States. - The United States produced in 1936, 4,800 tons per day or a total of 1,753,000 tons per year of sulfate pulp.

From plant practice (25), it has been found that the crude acids amount to approximately 2 per cent by weight of the pulp produced which would indicate about 35,100 tons per year as the possible production of fatty acids.

D. H. Killeffer (14), in a recent article, stated that since 1936 the production of pulp has increased 150 per cent which would mean a possible production of approximately 87,000 tons of fatty acids in 1933.

Increase in Value of Tallol by Distillation. - The crude tallol has usually been burned under boilers for its fuel value which amounted to only \$6.00 per ton. However, if the crude material is distilled for the recovery of the fatty acids and rosin acids, its value may be raised considerably according to the value of the refined material on the market. A few years ago its value was about \$80.00 (26) per ton when there was a great demand for this material, but in the last few years the demand for this product has

decreased with a corresponding decrease in market price. Depending on market conditions, any paper company that is refining the crude tallol should find a material increase in its income from the sale of these by-products.

Corrosion by Boiling Tallol. - Maurice de Eeghel (6), in 1927, stated that wrought iron, cast iron, copper, zinc, tin, and nickel vessels were appreciably attacked by boiling tallol after six hours' exposure while aluminum was only, slightly attacked. Of the materials tested by de Keghel, it appeared that a luminum was apparently the most suitable material of construction.

Corrosion Prevention of Copper in Fatty Acids. - A Cerman patent (1) claimed the prevention of corrosion of copper surfaces by fatty acids, especially acetic, by the addition of small amounts of substances such as H_2SO_4 , (COOH)₂, H_2SiF_6 , or base metal; these substances causing the deposition of any copper dissolved in the organic acid.

Corrosion of Lead Tanks by Oleic Acid. - G. O. Heyer (11), in 1933, found that lead lined iron tanks containing oleic acid had to be replaced after two years of service while lead lined wooden tanks lasted more than eight years. Laboratory experiments on corrosion of lead and lead-iron in oleic acid and water showed lead in contact with iron corroded more rapidly than lead alone, and hence the destructive agent was shown to be cleic acid lodging between the iron wall and its lead lining.

Use of 18 Per Cent Cr and 8 Per Cent Ni Steel. - In a discussion on the heat and acid resisting properties of steels, W. H. Hatfield (9), stated that 18-8 chrome-nickel steels were resistant to the hot liquid and vapors of oleic

and stearic acids. In a similar paper, J. A. Lee (17) stated that the addition of molybdenum to 18-8 steels greatly increased their resistance to organic acids. Maxwell (18) stated that the resistance of 26-3.5-1.5 chrome-nickel-molybdenum steels to fatty acids as oleic and palmitic was spotty but that it held up in some cases. This alloy has been suggested for use in seamless tubing in place of 18-8-2.5 Cr-Ni-Mo steel which has been found to be excellent in corrosion resistance but is not available in seamless tubing.

Iron, Chromium, and Molybdenum Alloy. - E. Baelecken (2), from a comparison of laboratory tests and actual installations found in 1937 that it was possible to avoid the use of nickel in preparing steel which is highly resistant to hot fatty acids in both liquid and vapor phases, by alloying iron with 17 per cent Cr and 1.5 per cent Mo.

Corrosion Tests in Crude Tallol. - Lilburn E. Mard (28), in 1937, tested a wide variety of metals and alloys for the corrosive effects of hot tallol. His results indicated that copper, nickel, aluminum, and their alloys, drome-nickel steels up to and including 18-8 steels were unsatisfactory because of their high corrosion rates. The result with aluminum does not agree with the result obtained by de Keghel (5) who found aluminum to be the only suitable material in his tests. Ward also disagreed with Hatfield (8) in the case of 18-8 chrome-nickel steels, for Hatfield had stated that these steels were resistant to the hot liquid and vapors of cleic and stearic acids. The difference in this case may have been due to the fact that Ward was not using pure cleic acid, but it was one of the constituents of his corroding medium

Ward found that stainless steels containing not less than 20 per cent Cr

and not less than 9 per cent Ni were satisfactory, with the most suitable one containing 29 per cent Cr and 9 per cent Ni. He also found that stainless steel containing 22 per cent Cr and 8 per cent Ni, and 18-8 steel containing 3 per cent Mo were satisfactory.

Tinder (23) in 1938, investigated several other alloys and found that the most suitable chrome-nickel alloys had compositions between 20-30 per cent or and 15-3 per cent Ni, and also that the addition of Mn had a favorable effect. In contradiction with this last statement, Speller (22) stated that the addition of manganese had no effect on the corrosion resistance of alloys. In Tinder's tests the 18-8 chrome-nickel steels proved to have good corrosion resistance which did not check with the results as obtained by Ward who found these alloys to have a relatively high corrosion rate.

Corrosion by Stearic Acid. - Kiichiro Kino (15), in 1938, investigated various metals and alloys in contact with stearic acid at 330-340°C, and found that German silver, silicon steels, and copper showed the least loss in weight. Nickel and ohromium, however, showed good resistance while aluminum, zinc, lead, duraluminum, wrought iron, steel, stainless steel, brass, cobalt, and tin were readily attacked. In another article, Kino (16) stated that bronze and nickel bronze exhibited the highest resistance to corrosion.

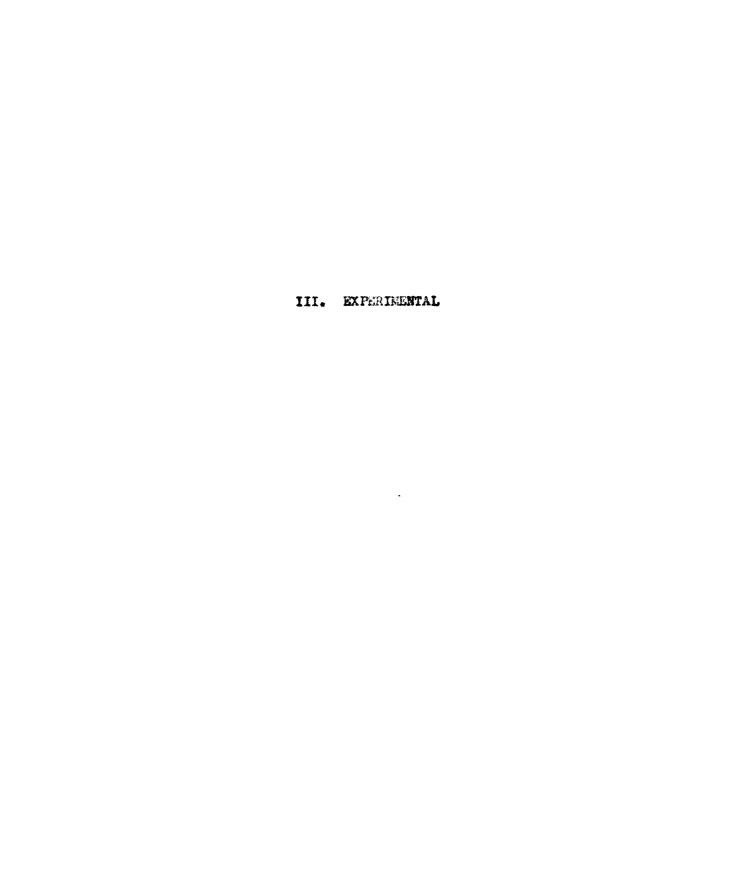
Alloys Used in the Soap Industry. - G. L. Cox (4), in a paper discussing corrosion of metals in the soap and allied products industries, gave some recent information on the alloys that were being used for distillation equipment. Inconel, an alloy of 79.5 per cent Ni and 13 per cent Cr had been used as a material of construction of a still and showed no appreciable corrosion after three years. It appeared that obsolesence rather than corrosion would

determine the useful life of this equipment. The 18-8 chrome-nickel steels with or without the addition of stabilizing elements had some application but were inferior to the 18-8-3 chrome-nickel-molybdenum steels. Monel metal, an alloy of 67 per cent Ni and 30 per cent copper was being used for bubble caps in distilling columns and for piping in the distillation and purification systems. While copper was used somewhat in this industry, it was being replaced by monel metal, for the copper corroded rapidly where the velocities were high as in pipe bends. Nickel Resist, an alloy of 14 per cont Mi, 3 per cent Cr, and 6 per cent Cu was being used in place of plain cast iron, for its resistance to corresion was 50-150 per cent greater than for plain cast iron. Even small amounts of certain alloying elements had a pronounced effect in improving the resistance of fatty acids. The addition of 3 per cent Ni with or without the addition of chromium doubled the resistance of cast iron, and these cast irons did not suffer graphitic corrosion to the same extent as plain cast iron.

Mechanism of Corrosion. - Vilbrandt and Ward (24) stated that since the fatty acids were non-conductors and the temperature of operation precluded the presence of water, the corrosion must take place by direct chemical action. In this case the action was controlled first by the diffusion of the fatty acids through an oxide film on the surface of the metal and then by the diffusion through the product of the reaction. Watts (30) concluded that all corrosion was electrochemical in nature.

Conclusions. - From the preceding experimental and actual plant tests, it can be seen that there has been little coordination of the corrosion data,

for the various investigators used different equipment, operating conditions, corroding mediums, length of exposure, temperatures, and means of preparing the samples. Since only a small percentage of the available materials have been tested for corrosion properties in hot crude tallol, additional work on this subject in an endeavor to find an economical, well-suited, resistant alloy seemed desirable.



III. EXPERIMENTAL

A. Purpose of Study

The object of this investigation was to determine the effect of alloying elements on the corrodibility of alloys of iron, copper, nickel, and aluminum in contact with crude tallol at 300°C, and the relative value of these motals and alloys for service under these conditions.

B. Materials

Corroding Medium. - The corroding medium was a mixture of fatty acids, called crude fatty acids or crude tallol, that was obtained as a by-product in the manufacture of kraft paper pulp. The tallol was composed of fatty acids, rosin acids, and unsaponifiable sterols and pitch. The fatty acids consisted of cleic, lincleic, linclenic, and related acids while the rosin acids were composed principally of abietic acid.

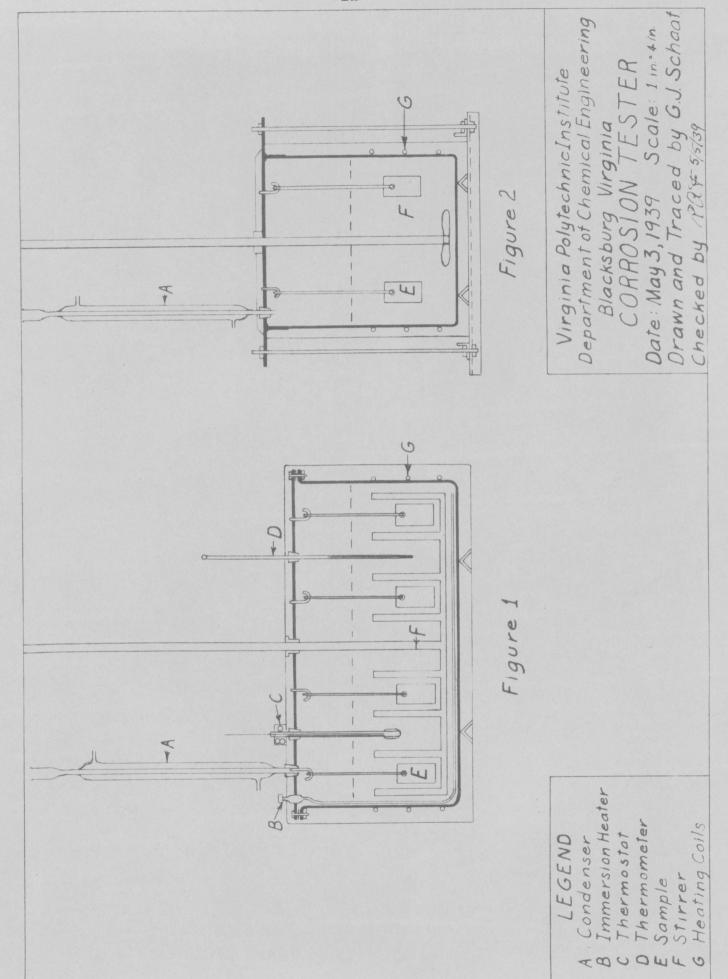
The alloys that were used in the tests were tabulated with their compositions in the tables 1 through 9.

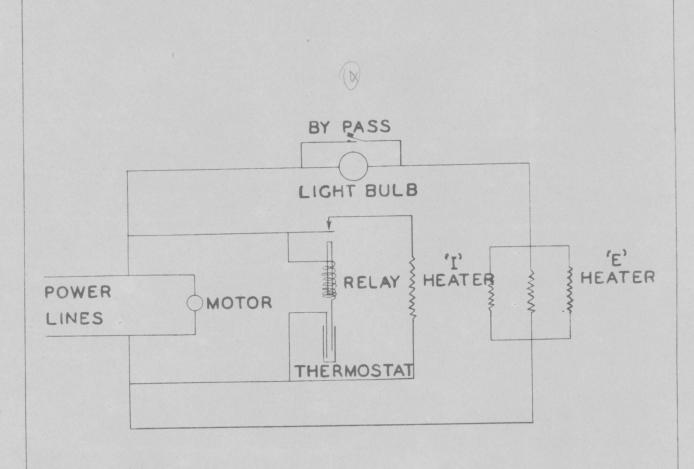
C. Apparatus

Three types of vessels were used to carry out the experimental corrosion tests on the various alloys.

Stainless Steel Kettle. - The first and most important testing apparatus is shown in figure 1. It consisted of a stainless steel kettle containing the corroding medium, a stirring mechanism (F), heating device (B and G), and thermostat (C) to maintain the temperature between 299° and 302°C. The stirrer (F) was first made by riveting strap steel blades to a steel rod, but this proved unsatisfactory as the rivets cofroded during the first twenty-four hours of testing. To overcome this defect the strap steel blades were brazed onto the rod, and this worked very efficiently. The blades of the stirrer were bent in such a direction as to cause a slow flow of the acids past the samples.

The heating device was divided into two parts. The first part (B) consisted of a 750-watt, stainless steel coated Aminco Lolag Immersion Heater with a 96-inch heating element which was obtained from the American Instrument Company. The second part consisted of three heating coils (G) insulated from the outside of the kettle by means of pieces of ceramic ware and covered with a thick layer of asbestos insulation. In heating the bath to 300°C both of the heaters were used, but when the temperature reached 300°C, the outside heater was turned off. However, this proved unsatisfactory for the radiation was too great for the capacity of the immersion heater so that another scheme had to be used. This was to place the outside heater in series with a 150-watt





VIRGINIA POLYTECHNIC INSTITUTE

DEPARTMENT OF CHEMICAL ENGINERING

BLACKSBURG, VIRGINIA

WIRING DIAGRAM

DATE: MAY, 3 1939 NO SCALE

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CHECKED BY A.A.F. 5/5/39

bulb after the temperature reached 300°C, and the heat supplied by the outside heater compensated for the radiation losses. The immersion heater was placed in a circuit with a relay and thermostat as shown in the wiring diagram. The thermostat (C) was a Precision Temperature Regulator, Model B, manufactured by the Fastern Engineering Company. Diphenylamine was used as the sensitive liquid, and the temperature adjusted at 300°C. By using the system of partial heating, the temperature was controlled within 2°C. In order to keep down radiation loss, the bettle was lagged with an inch thick layer of asbestos coment.

The stirring mechanism (F) was driven at 15 repeme by a $\frac{1}{4}$ He Pe motor with the necessary reducing gears, as shown in the photographs.

The samples were suspended from glass hooks which were in turn hung from steel hooks screwed into threaded holes in the cover of the kettle.

This method of suspension prevented the samples from touching each other or any other metallic part.

A condenser (A) was placed in the cover to return any volatilized acids to the kettle while at the same time acting as a vent for the non-condensible gases formed. The condenser was connected to a hood to carry away the gases formed which had a very foul, penetrating odor.

Incomel Ketule. - The second type of bettle that was used was fabricated from Incomel and the cover was made of an Incomel plated steel plate. In this case, the agitation was accomplished by a Monel propeller attached to a Monel rod rotating at 40 r.p.m. The temperature was controlled in essentially the same manner as the previous case, and the samples were suspended from the cover just as in the steel bettle.

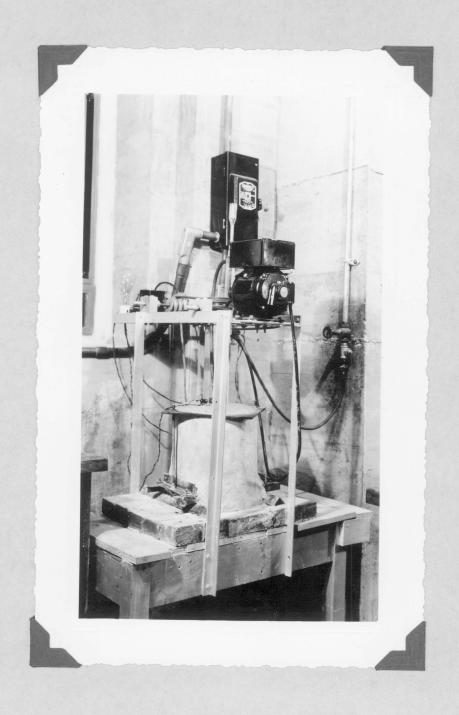


PLATE 1
Corrosion Testing Apparatus

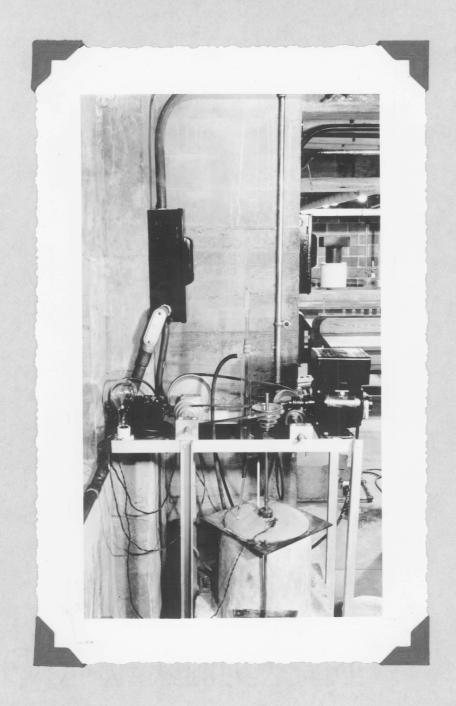


PLATE 2
Corrosion Testing Apparatus

The heating in this case was done entirely from the outside. Two of the resistance coils were placed in series with a 200-watt electric bulb to compensate for radiation while the third coil was placed in the circuit with the relay and thermostat. After regulation of the resistance wires, this method also kept the temperature within 200.

Glass Vessel. - The third type of vessel consisted of a well-insulated 500cc class flask. The heating in this case was accomplished by placing the flask on a hot plate and using the heater in the circuit with the thermostat. This method did not keep the temperature as constant as in the previous cases, for there was considerable lag in the heating and cooling of the heater, and in addition no agitation was employed.

Since this vessel could accommodate only a few samples, it was not used in any of the major tests, but only to determine the effect of acid number on the corrosion rate.

D. Method of Procedure

Preparation of Samples. - The samples were cut or ground to approximately one inch by two inches, the rough edges filed off, and a small hole drilled in each sample so that it could be suspended from the glass hooks. The samples were then washed with benzene to remove any oil from the surface, dried with a clean cloth, and then carefully weighed. The dimensions of each sample were measured using a magnifying glass and a hundredth-inch steel scale.

No special treatment was given to the alloys except the welded samples, for it was desired to approximate plant conditions as nearly as possible. Due

to the cutting, there were probably some strains set up in the edges of the metal, but the alloys were not annealed to remove them.

The welded samples, which were about 2 x 2 inches in size, were out in half by a machining tool and any rough edges machined off. One piece of each welded alloy was machined smooth so that the inside of the weld would be subject to attack by the hot fatty acids.

Final Treatment of the Samples. - At the end of each run, the samples were washed twice with bensene and wiped clean with a clean cloth. After weighing the samples, they were examined for pitting that was visible to the eye. No attempt was made to evaluate the depth of pitting.

Pirst Test in Stainless Steel Estate. - After placing seven gallons of tallol in the stainless steel vessel, the tallol was heated up to about 100°C, to change it from a thick, viscous mass to a thin liquid. Then the samples were inserted and the cover lowered upon the kettle and bolted fast. The stirring device was them set in motion and vigorous heat applied to bring the temperature up to 300°C. In the first run the regulation of the heating devices was necessary, and consequently, the temperature varied rather widely. At the end of twenty-four hours, the heat was shut off and the samples removed, cleaned with benzene, dried, and carefully weighed. After this the samples were returned to the kettle and the heat applied again to raise the temperature to 300°c. By having a partial heating from the outside, the temperature was held fairly constant until a drop of mercury stuck in the terminals of the thermostat and shut off the internal heater. The time could not be taken accurately for this reason, and the results of the first run cannot be considered to have a high degree of accuracy.

Second Test in Stainless Steel Kettle. - In the second run, however,

suitable operating conditions were found so that the temperature remained at 300°C 2 2°C during the entire run.

Third Test in Glass Vessel. - In the third run, which was performed in the glass vessel, no difficulty was encountered except that the temperature varied about 24° from the desired temperature of 300°C.

Fourth Test in Income! Kettle. - The fourth run ran smoothly until the heating wire burned out and hence only a twenty-four-hour run was made.

Since this was a comparative run to determine the relative effect of stain-less steel and income! kettles, the results were comparable at twenty-four hours.

Decrease in Acid Number. - An acid number was taken at the beginning and end of the first run. About one gram of the acids was dissolved in 50 ec. of ethyl alcohol and titrated with standard alkali using phenolphthalein as an indicator. Considerable trouble was encountered in observing the end point, for the solution was dark brown in color. The solution was diluted with more alcohol, but the end point was no easier to determine. The acid number was calculated as the number of milligrams of potassium to neutralise one gram of the acid.

Corrosion Rate Formula. - The method of operation of this test was an adaptation of the standard static corrosion test as outlined by Perry (20). In calculating the corrosion rates, the formula given in Speller (21) was used for all cases. The formula which gives the rate of corrosion in inches per year, was as follows:

where

P-Rate, in inches penetration per year
W--Loss in weight in grams
S--Specific gravity
T--Time in hours

E. Results and Data

Arrangement of Tables. - Table 1 gives the trade name, specific gravity, manufacturer, and sample numbers of the specimens used in the first run. The sample number is used to refer to the compositions and rates of corrosion given for the first run in Table 2. Table 2 gives the compositions of the alloys tested in run 1, the data necessary for the calculation of the corrosion rates and the corrosion rates for the twenty-four and seventy-two hour tests of run 1.

Table 3 gives the trade name, manufacturer, specific gravity, and alloy numbers of the alloys tested in runs 2, 3, and 4.

Table 4 gives the corrosion results for the twenty-four and seventy-two hour tests of the iron alloys that were tested in run 2. Tables 5, 6, and 7 give the corrosion results for the twenty-four and seventy-two hour tests of the nickel, copper, and aluminum alloys respectively that were tested in run 2.

Table 8 gives the corrosion results of the two alloys tested in order to determine the effect of acid number on corrosion rate in run 3.

Table 9 gives the corrosion results for the twenty-four hour test of the nickel alloys that were tested in the inconel kettle in order to determine the effect of the composition of the kettle on corrosion rates in run 4.

Table 1

Manufacturers of Samples Used in Aun 1

Sample Number	Tre	ide Name	ã° e	nufact	arer		Specific Gravity
1		A =33	Alleghen	7 Steel	Compan	y	7.64
2		2-44	ñ .	• •	**	•	7.90
3		A-55	98	ft	:1		7.80
4		A-66	14	tt.	**		7.70
0 5		307	tt .	71	11		8.02
0 6		307	17	##	11		8.02
0 7		316	#	Ð	19		8.06
0 8		317	£ 9	17	a		8.06
0 9		347	it	11	11		7.97
×10	iast	elloy A	iaynes-	-Stell1	te Co.		8.80
*11	*****	B		11	n		9.24
*12		it G	ft	rf	* *		8.94
13		1	American	hollin	g 1111 -	ാറം	7.90
14			n	#	·	ii T	7.93
15		3	11	++	Ħ	:0	7.93
16		2 3 4 5	44	11	n	H	7.93
17		5	49	ti .	86 :	13	7.93
18		6	t†	Ħ	11	H	7.93
19	Alane	53-3-7	Aluminum	n Co. o	f Amonto	20	2.69
20	11200	99.4	#	11 11	et .	Ju	2.72
21	ezista		Grucible .	itael 3	o. of A	maria	
22	11	7	01.00.00.00.00	11 11	, ii	tt To	7.72
23	#	4	tt	\$7 9 6	ŧŧ	# F	7.84
24	!	XA 25 So	n	27 50	15	78	7.91
25	11	12	17	11 (1	15	21	7.76
26	tt.	17	\$ †	et ft	51	59	7.70
27	16	24	**	tt tt	11	11	7.65

^{*} Cast Metal

o Welded Alloys

Table 1
(Continued)

Manufacturers of Samples Used in Run 1

Sample Number		Manufacturer	Specific Gravity
¥28	Zorite	lichiana Products Co.	8.05
¥29	Alloy 48	if it th	7.75
30	ŠOŠ	Carnegie Illinois Steel Corp.	7.91
31	316	ti it i	8.05
32	3 09	49 91 92 97	7.83
33	446	86 86 38 19	7.47
34	Nickel	International Nickel Co.	8.85
35	Monel Metal	18 50 10	8.80
36	Inconel	# # #	8.55
_	Enduro 18-8-5-No	kepublic Steel Co.	8.05
38	" 18-8-S	n ii ii	7.98
#39	Duriron	The Duriron Co.	7.00
40	18-8-%o	Source Unknown	8.05
41	17-7	t fi	7.90
42	18-8	ti tf	7.93
*43	CN-2	Goneral Alloys Co.	7.85
44	Angle Iron	Source Unknown	7.83

*-Cast Metal o-Welded Alloys

Table 2

nun 1-Corrodibility of Various Alloys in Crude Sallol

*-Cast Wetal o-welded Alloys

able 2

(Continued

hun 1- Corrodibility of Various Alloys in Grude Tallol

		P1 ts	919		yes	yea	8).	Nes	31.	<u>4.1.</u>	0	763	81.	801	768	89∆	3.08	VOS	New Y	86/	Yes
		Scales	ç	2	yes	80/	yes	V 03	no	no	300	yes	ou	V 60	yes	yes	yea	yes	30 A	80 Y	80A
Test	a te	in./yr.	0.0065		2000	6800*0	0.0107	0.0112	0.0116	0.0129	0.0217	0.0226	0.0300	0.0394	0.4580	0.5060	•	0.5825	•	8	
54 hour	t. Loss	gr a •	0.0143	,	•	•	•	•	•	•	•	•	•	•	•	1.9131	•	•	•	•	•
rest	na to	in./yr.	0.0228	•	•	•	•	•	•	•	•	•	•	•	•	0.7415	•	•	က္	43	1.78%0
24 iour	t.Loss	E 238 .	0.0222				•		•	0.0048	•	•	0.1045	•		•	•	•	1.4203		1.0319
Aros of	Sample	sq. in.	4.3190		•	•	•	4 .2770	•	5.3080	-	•	લ્યુ	4 .2 100	4.6420	0638.♦	€ . ∵570	4.2140	4.5390	.17	2.5570
		Others	0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0		100) 	n- 1.0			In- 0.4	Ca-30.0	lin- 0.4			En- 0.4	En- 1.0			3.0 -u		
ton	93	# 1) :	?	0		+=====	4.0		O လ		+	4.	4.0			4.0		
Composition	Percontage	္က				*	*			***		1			1	* * *		-			
Con	Per	73	8.0	a		9. 9.	35.0			11.7		က တ	•	W.	O Oš	0			7.0	* * * *	
		ż	18.0	10.	-		•		্	o.		-	18.0	-	-	-	0° %	0.07	15.1	12.0	+
		9.5	391.			N.	38.1.	<u>.</u> :	: 1	E	7.7	.41.	= :	ε :	- :	Ε.	= ;	E;	Z: :	E	٠. ن
	Sample	Number			3 :	\$		33	cy Cy	ပ္	გე დ	2	ထ္ထ	႙	4	ĸ	27		 4	C3 U3	4

*-Cast Setal o-selded Alloys Tempersture sange: 280°- 310° G. Corroding Sedium: Grade Fatty Acids

Stainless Steel Nettle Used

Table 3

Wanufacturers of Samples Used in nuns 3 & 4

Sample Number	Trade Name	Manufac	turer			Specific Gravity
1 2	Groloy 5	The Babcook	: & #1]	cox ្ពំព	be ço.	7.80 7.30
3	hezistal 12	Grunible Ste	al Co.	of Ame	anias	7.75
4	17	Crucible Ste	11	H 62 52 52	H TOW	7.72
5	" 24	ff 9	11	11	n	7.65
6 7	" KA2	ft <u>9</u> 1	e e	17	**	7.94
7	11 4	ri ti	11	ti.	11	7.84
8	¹¹ 7	11 11	£t	11	f 3	7.72
9	" A2STo	# #	#	79	13	7.91
*10	Alloy 48	Lichia r	na Prod	unta Co		7.75
#11	49	** Action	11 OC	lucts Co	J •	7.70
#12	n 100 S	Ħ	**	**		7.87
#13	1 122	41	11	ti		7.89
*14	Zorite	> }	fI	11		8. 05
15	302	Compania 13	Manda	C to a 1	3	
16	316	Carnegie 11	TITOTA	11 2 COGT	oorp.	7.91
17	309	ę y	11	18	n	8.05
18	446	er e	n	11	(1	7.83
19	1	American	olling	. 20433	٧	7.47
20	2	WESGI, TOWIT	OTTTUE	1411 F		7.90
21	3	T)	tt	11 :	7	7.93
22	4	11	† 1	H t	•	7.93
23	5	Ħ	11	ft :	1	7.93
24	6	11	#	B (1	7.93
25	A -33	4 7 7 m 1s				7.93
26	A-44	$\mathbf{Allo}_{\widetilde{\mathcal{G}}}^{\bullet} h$	eny St	eel Co.	•	7.64
27	Λ-55	fŧ		17 55		7.90
		t)		п н		7.60
28	A = 66	11		17 51		7.70
029	307	£\$		11 12		8.02
o 3 0	307	ti		ti ii		8.02
031	316 216	**		17 18		8.06
032	3 1 6	Ħ		11 17		8.06
o33	317	(*		tt 11		7.97
034	317	11		TT 11		8.06
035	347	ti		11 11		7.97
o3 6	347	17		**		7.9 7

^{*} Cast Metal

o Welded Alloys

Table 3 (Continued)

Manufacturers of Samples Used in suns 3 & 4

Sample Number	Trade Name	Manufacturer	Specific Gravity
*37	Q Alloy A	General Alloys Co.	8.05
43 8	Q Alloy B	" "	7.94
~39	Economet	H H H	7.78
440	C-1	i7 11 39	7.60
41	CN-1	şi 11 11	7.90
42	CN -2	17 (6 §2	7.85
*43	X-1 to	\$\$ 94 \$\$	8.05
444	Hastelloy A	maynes Stellite Co.	8.80
445	" B	H H	9.24
	" G	33 45 14	8 .94
47	N1chrome	Driver-harris Co.	8.36
48	dichrome V	n n	8.41
49	Mirex	77 11 11	8.5 5
50	Monel	ts	8 .80
51	Inconel	International Nickel Co	
52	Nickel	H H	8.3 5
53	Z Nickel	tt tt	8.85
54	Fonel	n n	8 .80
55	K Monel	14 11 11	8.6 0
¥56	Mi Mesist (Ou free)	\$\$ \$\$	7.55
\$57	Mi Lesist	H H H	7.55
58	Alcoa 25-gH	Aluminum Co. of Ameri	ca 2.71
59	" 33-gH	a n n	2.73
60	" 52S - žn	\$\$ \$\$ £\$ £\$	2.67
61	99.4	n n n	2.72
62	" 53-S-W	a t ii ii	2.69
#63	40 Alloy	National Smelting Co.	2.77
≈64	12 S Alloy	11 11 11 11 11 11	2.64
#65	40 M Alloy	79 gg gg	2.63
* 66	5 S Alloy	18 15 11	2.66
6 7	Chromium Cu-S	American Brass Co.	8.90
68	Chromium Cu-h	и и	8.90
69	Ambrac 850	H H	8.86
70	Og free Cu	Phelps-Dodge Copper Co	. 8 .94
71	Duronse II	Bridgeport Brass Co	
72	Duronze III		7.69

^{*} Cast Metal

o Welded Alloys

Table 3 (Continued)

Sample Number	Prade Bame	Man	ufacture	er .		Specific Gravity
73	mills-NcCanna 45	Hills	-MoCanna	Co.		7.50
74	" " 52	18	Ħ	Ħ		7.80
7 5	" 102-P	\$1	11	ri		8.55
76	Commercial Bronze	Revere	Copper	& Brass	Co.	8.81
7 7	LOW Brass	7t	W	n	11	8.66
78	Seventy-Thirty	Ħ	Ħ	it	₹₹	8.52
79	buntz Fotal	n	**	91	F \$	8.42
80	Phosphor Bronze	17	Ħ	17	Ħ	8.85
81	Admiralty Metal	17	n	77	† ‡	8.52
82	herculoy	17	91	11	19	ુ.52
83	Copper	13	\$1	件	tt	8.92
84	Phosphor Bronze	31	16	Ħ	Ţŧ.	8.81
85	Strap Steel	So	urce Unk	cnown		7.83

#-Cast Metal o-Welded Alloys

Table 4

Run 2-Corrodibility of Various Chrome & Chrome-Mickel Alloys in Tallol

Sample			Compo	81t1 ntag	on		Area of	24 Hour	r Test	72 Sour	r Test		
Number	FIG	Cr	I	0	u,	31	9q. in.	gra.	in./yr.	ETS.	in./yr.	Scales	P1 ts
	Ea 1.	3	13.9		-1.5	•			0.0000	0.0000	000000	no	ou
1 3	=	23.8	10.4		8.0	٥ . ٥	4.1891		•	000000	000000	ou	000
	.	.	0	•		•	•		•	•	00000	ou	000
	Ŧ :	ග		ς, Φ	•	•	•	•			•	ou	00
O)	*		ပ	•			•	•		•	0.0001	000	ou
2	.	•	ញ	ı			4.9233	0.0010	•	•	0.0002	91.	no
0 %		•	•	හ හ				•	•	•	0.0002	02	20
%	= :	18.8		٠	1.4	0 0	•	6000.0	9000.0	•	0.0002	8	000
9	S	•	10.4		1.1		•	0.0005		•	0.0002	ou	000
<u>ං</u> 36	£		•	•			•	0.0011	900000	•	0.0002	ou	2
0 33	<i>i</i> . :	Ġ	i	3.9	1 1		•	0.0012	9000.0	•	0.0003	no	00
	: ;	17.5	ei ei	ာ း			•	0.0000	0.0011		0.0004	on	ou
ထ	E	ιΩ	80				•	0.0020	0.0013	•	•	Sey.	ou
	-	Ġ	111.7	+====	* * * * * * * * * * * * * * * * * * * *		•	0.0021	0.0011	•	•	013	000
	502	31 t		inknown			5.4521	0.0023	0.0012	•	•	ou	من
o 30	2	o O	•				•	0.0028	0.0015	•	•	no	no
	= :	•	12.7	Ož Ož			•	0.0026	0.0015	•	0.0006	ou	<u>0</u>
20	£ :	Ġ	•				•	0.0028	0.0019	•	900000	ou	31.
의 ※	2	28.0	ං හ		ල. ට	0 8	•	0.0055	0.0026	•	6000.0	81.	۰.
0 35	£ :	ຕໍ	11.0			****	•	0.0039	0.0021	•	0.0000	ou	ou
C4 C3	.		•				•	0.0061		•	0.0013	ou	81.
*		•	ය. වෙ	3	1 1		•	0.0114	00	•	0.0017	763	Çva
÷O		•		1			•	0.0068	0.0050	•	0.0017	763	81.
21 *	æ	ຜ່	0.21		3.5	1.3	•	0.0153	•	•	0.0027	yes	2
	z.	19.0	38.85	1			5.7689	0.0187	0. 0038	•	0.0031	yea	2.
\$ %	5	10.0	30.0				9000.9	₹	0.0105	0.0213	0.0033	уев	3 . .

Table 4

(Continued

Run 2-Corrodibility of Various Chrome & Chrome-Sickel Alloys

	P1 ts	<i>></i>	2**	81.	800	٠ <u>٠</u>	پ	ç.	V 08	7 88	Yes	¥08	Yes	80 A	Y 68	gue •	Yes	yes	yes
-	Sca 168	80A	Ves	00	no	Ves	S⊕>	V63	60	8 0 A	802	ves.	8 0∧	¥08	A G G	798	уев	yes	yes
2	in./yr.	0.0035	0.0042	_	0.0066	0.0079	0.0105	•	0.1236		•	•	•	0.4524	•	•	•	.14	•
72 cour	Era.	0.0191	0.0231	•	0.0361	0.0481	0.0530	0.1386	0.6016	•	1.4510	•	•	2.1299	4	•	8996.2	•	6.3009
Tost	in./yr.	\$600.0		0.0130	9610.0	•	0.0383	0.0746	53		0.7490	•		1.1410	0018-0	•	•	80	2.7680
24 1001r				0.0196	0.0355	•	•	•	0.6122	•	•	•	•	•	•	•	u)	. 14	4.5179
Area of	8q. In.	5.0133	•	4.1891	•	•	•	•	4.6522	•	•	•	•	•		S. S	3.9816	္သ	<u>ග</u>
	31	1		0 E		0.1	*	ာ	1		4.0	α Ο		ֆ .	· •	*			o ••
c	u	8.0	* * * *	4.0	4.0	7.0	own -	ය. 0		4.0	0.1	ر. ت		4.0	₹.	· uno	1 1 1 1	1	4.
Corposition	0.7		* * * * *	+	+	***	Unknown	+====	1 1	+	+ 1 1 1		+ = = = =	1.7	+ 1011	Unknown		+ + + + + + + + + + + + + + + + + + + +	<u>်</u>
Correct		12.0	67.0	0 0	7.9	38.0	ittion	<u>ා</u> ස	1 1	o C	4.0	* * * * * * * * * * * * * * * * * * * *			0.1	1:10n	+ 1 - 1		
	r.	25.0	20.03	18.3	30.5	16,0	Composition	18.5	0. 58	16.3	12 13 13	ය. ව	17.0	0.7	15.1	Compost	<u>্</u>		ro cs
	9.3	.a.1.	=	2	E	-	=	=	z :	C	= :	= :	- ·	: :	= 1		<u>.</u>	- 66	-
a Lumble	Nurber	× 41	i 37	18	(C)	× 14	\$ 3B	*	മ	ଝ	27	87	ব্য	C)	(N (D	0 ₩	n	က ထ	~4

*-Cast Febal o-Welded Alloys emperature ange: 2990- 3020 c. Corroding Fedium: Orudo watty Acids ?-Unable to ascertain Stainless Steel Kettle

Table 5

Hun 2-Corrodibility of Various Mickel Alloys in Grude Tallol

Percentage	Composition Percentage			Area of	24 hour	r Jest	72 Our	r Post	
Si Others		othe	P. S	sq. In.	gra.	in./yr.	grs.	in./yr.	Scaling
4 2 9 4 2 9 4 4 4 4 4 4 4 4 4 4 4 4 4 4		1 1		4 .3202	0.0008	0.0001	90000	0.0001	Ş
3		0	*		0.0001	0.0031	0.0071	0.0018	2 €
-	* * * * * * * * * * * * * * * * * * *	\$	ာ ၁	4.4666	0.0086	0.0049		0.0017	OL
	1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	ŧ	1	4.4521		0.0065	0.0127	0.025	81.
S S . S .	10 00 01		3	•	•	0.0043	0.0134	0.0025	ou
·0 No-23	-	2-0g	့	4.7941		0.079	0.0190	0.033	. E
8 0.1	T. 0	***			0.0191	0.0105	0.0202	0.0037	yes
10-33	*	() ()	3.0			0.0079	0.0201	0.0044	91.
<u>်</u>	0.1		1		•		0.0348	•	yes
0.1	0.1				0.0280	0.0154	0,0649	•	yes
1	****			•	0.0388	0.0218	•	:013	805
1	S			4.6311	•		0.0755	0.0135	yes
	1.7	9		-	0.2846	0.1222	0.3901	0.0566	£ 6 3
ಲ ಜ಼ ಗ		S S S S S S S S S S S S S S S S S S S	ದ್ದು	ය. රූපුරුණ අදුරු	0.7012	0.3061	C.000.0	0.1440	80%

lemperature .ange: 2990-3020 C.
Corroding ledium: Crude Matty Acids
%-Usst Fots!
No Visible Pitting
Stainless Steel Kettle

Table 6

Hun 2-Corrodibility of Various Copper Alloys in Fallol

		2-21																		
		Scoling	BUA)) ::	¥	•	=	*	C	*	2.	t	=	:	£	=	£	=	z	#
r Test		in./yr.	0.000	0.0001		0.0082	160000		0.0130		0.0148		0.0152	0.0165	0.0203	0.0236	•	0.0635		•
72 Hou	Wt.Loss	€ 28.	0.000	0.0004	0.0073	0.0475			•			0.0382		0.000	0.0765	0.0393		0.0104	0.3420	
r iest	in to	in./yr.	0.0019	0.0028		0.0270		•	0.0274	0.0399	•	0.0352	0.0399	0.0114	0.0305	-	0.1009	0.0886	•	0.4100
24 Hour	ot.Loss	gr s.	0.0031	0.0054	0.0087	0.0443	0.0497	0.0420	0.0464	0.0690	0.07777	0.0297	0.0821	0.0208	0.0500	0.0218	0.0803	0.1471	0.3157	0.6304
free of	Samp1e	sq. In.	4.1989	4.6905	4.3038	4.2199	4.4276	4.2408	4.1838	4.8040	4.3087	2.3717	5.2873	4.6905	4.0407	•	2.3299	4.7355	4 •3∂68	4.0148
		others		******		1 1 1 1 1	11-20.0		Cr- 0.9		****	M1-16.5	***************************************		Cr- 0.9	F8- 1.8	0.1 -0.			
no	9	Sn				()	*			7.3	4.0		0.8							
Composit:	Percentag	31	-			ය ග			0.1		1	1		() ()	0.1	4.0		0,00		
Com	Perc	7 %			****		1 1	***				0.6	2				10.0	7.1		
		Zn			10.0	ာ ()	رت 0	20.0	1 1	2.0			27.7			1.5			30.0	40.4
		Cu	6.66	6.66	•	96.1	75.0	8 0. 0.	99.1	98.8	0.06	74.5		97.3	99.1	3, 26	0.68	91.0	70.0	3° 89
	Sample	umper	33	8	76	88	69	77	සු	84	<u>0</u>	%	81	7	67	32	5	72	78	79

Temperature ange: 299°-302° C. Corroding edium: Crade Maity ficids Stainless Steel Kettle

Table 7

Hun 2-Corrodibility of Various Aluminum Alloys in Crudo Tallol

			Comi	Composition	8		Area of		24 Hour Test	72 Hou	72 Hour Fest	Scaling
Sample			Perc	Percentage	9		Sample	WE . LOBB	in to	1t. LO38	Eate	or
Humber	Al	7	3	Ça	r.	Others	89. in.	gra.	in./yr.	Era.	in./yr.	Pitting
	93.5	0.8		₽.Q.		r'a-0.3	5.3023	000000	00000*0	0.0000	000000	auou
64	87.7	11.9	1 1 1	0-1	0.1	.1 80-0.3	E • 4 5 5 2	00000	000000	000000	00000	none
e e	95.1	0	(N	က က	0	Part. 3	£0000 3	0000°0	000000	0000:0	00000	none
ත ග	98.8		1 1 1		-1.2		4.0728	6.0017		0.0025	0.0016	none
	6.66	* * * * *			1 1		4.0485	0.0021	0.048	0.0029	0.0019	none
	97.8	0.7	1.3+		1 1 1	Or -O - 3	4.5858	0.0021		0.034	020000	none
	95.0	رت د .		0.1	0.1	0.1 Fe-0.4	5.3368	0.0028		0.0044	0.0023	ncne
61	29.4			1 1 1 1			4.0702	0.0030	0.0058	0.0071	0.0041	none
	97.5	2	2.0	****		* * * * * * * * * * * * * * * * * * * *	₹.0095	0.0046	0.0094	09000	0.0040	none

Temperature Lange: 2990-302° C. Corroding Modium: Crude Fatty Acids 4-Cast Detal Stainless Steel Kettle

Bolo 8

Run 3-%ffect of Acid sumber on the Corresion unte

	S	Composition	ton	Aros of	Area of 34 Jour rests	r ests	ela:ive	P#4
	Pe	Percentage	Ве	Sample	#t . Loss	ate	co reston	pag.
irade Name	E.	1%	r.	8q. In.	Era.	in./yr.	ate	
Ornalble 410	. L. W.	0.21	0.51	02 20. \$	4.6320 3.3243 2.3320	2.3320	1.336	42
Indaro 18-8	*	0.8 0.8t	ං ස	4.1780	4.1780 0.0065 0.0043	0,0043	040	2.75
Crasible 410	E	12.0	0.81	06.40.4	4.0430 2.4370 1.7490	1.7490	1.000	٥
nduro 18-8	=	18.0 8.0	0.8	3.1250	3.1250 0.0012 0.0011	0.0011	1.0 50	O

* First 24 Jours

o Second 24 Lours Corroding Sedium: Urude Patty Acids Sempsrature Lange: 2980- 3050 J. Acid Surber: Start 152, After 24 Lours 95, After 48 Lours 50.

Glass Vessel Used

Table 9

Hun 4-Corrodibility of Various Hokel Alloys in Fallol

		, de	4 4 6 7 7	1		4	4		
		05	00: 081 t10u	Tou		10 W. T.	71:0: 45	T 163 L	
Sample		Pa	Percentage	63		Sample	it. Loss	a to	
ber 11	Cr	ηŋ	6	31	Othors	3q. fm.	grs.	1n./yr.	Scaling
G	00					67 7	0000	2000	3
•	_				000	*	•	₩.	CI
	0 13.0	1 1 1	٠ د د			~# ~	0.0088	0.0007	no
•	00000	1 1 1	1 1 1 1	1 1 2	0.0	4.4697	0.0000	350.0	91.
79.5	3 13.0	က	න ආ	(1)	1 1 1 1 1 1 1	4.7159	0.0071	02000	О Ц
•		1 1	0.23	1	0.83-0	4.0200	0.093	3500.0	81.
•	1	1	7.0	1 1	0.00-01	4.7072	0.0111	0.0055	s.j.
30.0	0. 1:1	1	0.0	1 1	1 1 1 1 1	K N		0.00EG	ou
	1 1 1	0.1	α. •	0.1	1 1 1 1 1 1 1	4.6320	0.0151	0.0000	80
		20.02	<u>ာ</u>	7. 0	1 1 1 1 1 1 1 1 1	4.8170	0.0162	3 OO. O	308
		 	2.0	1 1 1	1 1 1 1 1	4.6709	•	070 0.0	yes
•		30.00		1 1 1		ঝা	0.0199	0.0115	808
•	0	30.0	1.4	S. 0			0.0213	0.0112	80%
14.6	(3)	ক ত	70.5	1.7	•	7.0019	0.3646	0.1514	yes
		1 1	ري وي	CQ —	ದ <u>್</u> ಚ	6.0854	0.4562	0.1982	708

Temperstare wange: 289°-302° c. Corroding Fedium: Grude Fatty Acids *-Cast Fetal No Visible Pitting Inconel Aettle Used IV. DISCUSSION

IV. DISCUSSION

Comments on Procedure. - In reviewing the procedure that was used in the corrosion tests it seemed advisable to consider the possibility of making some changes. It was noticed that the acid number decreased rapidly during the test runs, and experiment proved that this had a large effect on the corrosion rate. Since the acid number decreased from about 150 to 90 during the first twenty-four hours, it did not seem feasible to change the acid bath during the tests, for this would necessitate a number of changes even for a twenty-four hour run and give a non-continuous effect.

It was not advisable to lower the temperature to prevent lowering the acid number, for this would not give the effect that is obtained in the plants. It was shown by run 5 that the decrease in acid number resulted in a decreasing of the corrosion rate to a very considerable extent, and hence it would be desirable to modify the testing method in order to approximate plant conditions. One means of accomplishing this purpose would be to operate the tests with a continuous cycle of hot fatty acids. This method would require a large quantity of material, however, and at the same time cause many difficulties in operation.

Therefore, it seemed advisable to continue with the present method of operation and obtain the relative corrosive effect of the hot, crude tallol, and after these effects had been observed, the better materials could be tested in plant equipment to obtain the actual corrosion rates.

Some of the samples tested formed films on the surfaces which could not

be removed with any solvent which would not attack the metal itself. One method that has been used with considerable success in some cases was to remove the film by abrasive method. Before this method can be used, however, the error due to its effect must be known. No attempt was made to utilise this method in the final preparation of the samples.

Control of Thermostat Lag. - After regulating the heating elements so that the temperature remained constant, no serious difficulty was encountered in the operation of the equipment. Care had to be taken with the thermostat so that a bit of mercury did not stick between two terminals and shut off the heat. However, when a layer of lubricating oil was placed over the mercury, the "sticking" effect was eliminated.

Theory of Corrosion with Fatty Acids. - F. C. Vilbrandt and L. E. mard (24) have stated that since the acids were non-conductors and no water was present, the corrosion took place by a direct chemical mechanism. The rate was controlled by the diffusion of the corroding agent through an oxide film on the surface of the metal and then by the diffusion through the reaction product.

During the present tests exidising conditions may have existed even though precautions were taken to minimise the smount of exygen that came into contact with the fatty acids. A number of samples had strongly adherent scales that appeared like exides; however, there is more possibility that the scales were salts of the fatty acids.

Effect of Acid Number. - The third test was run specifically for the purpose of determining the effect of acid number on the corrosive properties

of the fatty acids. Two test samples, one of 18-3 chrome-nickel steel and the other of 12 per cent chrome steel, were subjected to the corresive effects of the fatty acids at 300°C. for twenty-four hours; and after these samples were removed, two similar fresh samples were tested for twenty-four hours in the same acid. In the case of the plain chrome steel, the corrosion rate decreased to 25 per cent of that in the first twenty-four hours. For the 18-8 steel, the rate decreased to 25 per cent of that in the first of that in the first twenty-four hours. These results indicated that the corrosion rates obtained in these tests could not be considered as absolute values.

Effect of Kettle Composition on Corrosion Rate. - In order to determine the effect of the kettle's composition on the rate of corrosion of the samples, test 4 was run for comparison of an Inconel kettle with a stainless steel kettle used in test 2. In test 2, several nickel samples were placed in the stainless steel kettle along with the other samples while in test 4, only nickel alloys were used in an Inconel kettle using a Monel stirrer. The results indicated that the composition of the kettle had no effect on the corrosion rate or the relative rates of corrosion of the nickel alloys. This should be repeated with nickel alloys and steel alloys in the Inconel kettle.

Effect of Cold working. - In the method of preparation of the samples, the rough edges were filed off, and this instituted some cold working strains in the metal which were important in the case of the stainless steels. After the samples were tested, some of the specimens showed that

at the file marks there was noticeable pitting while in the other portion of the metal these effects were not noticed.

However, in the preparation of the welded alloys that were machined smooth, which is another form of cold working, there was no pitting that was noticeable to the eye.

sawed in half and filed smooth. After testing for their corredibility in the fatty acids, the welds showed attack especially at the weld. Even in the sample in which the weld bead was not filed off, the weld showed slight signs of pitting. In this test the 18-8-3 Mo steels, which were not filed, showed no signs of attack. In the second test, in which one section of the welded alloy was machined smooth, no pitting effect was noticed. However, in some cases, either the weld or the surrounding metal was stained a slight bronse color. The cause of this may have been due to staining by the fatty acids or their decomposition products, or to the precipitation of some metallic element or compound on the surface of the iron.

Effect of Films on Stainless Steels. - One of the cutstanding characteristics of the chrome-nickel steels is their resistance to exidising conditions. The cause of this resistance effect is said by Bain (3) to be caused by the formation of an exide film which is repaired almost instantaneously when broken. The chrome alloys also exhibit this effect but to a much more limited extent than the chrome-nickel alloys. The presence of molybdenum (24) aids in the formation of a more impervious film and also improves the resistance of 18-8 steels to intergranular corrosion to which the 18-8 steels are susceptible.

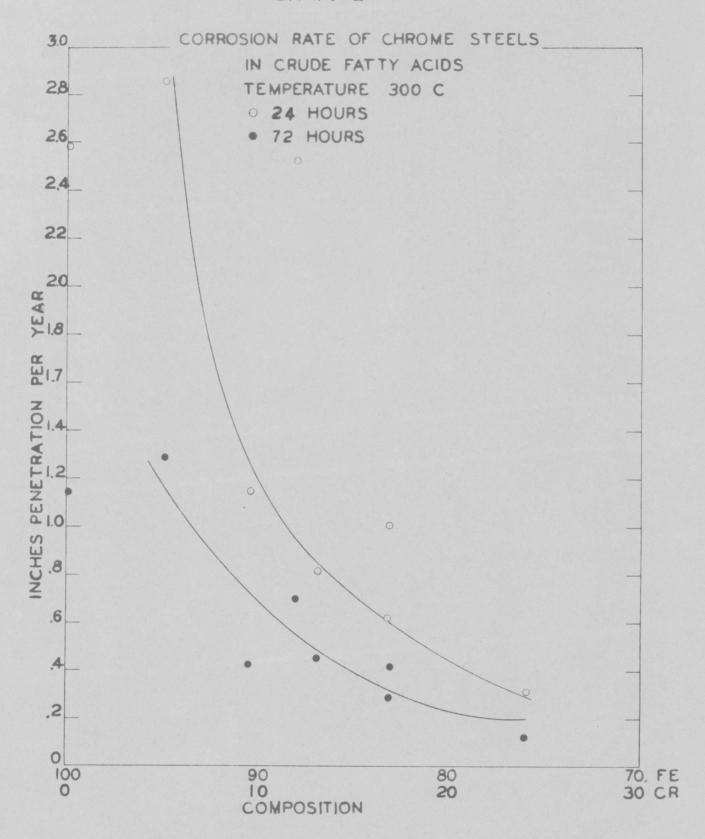
The protective power of a surface film is relative, according to Hedges (10), Evans (8), and Johnson (13), and depends upon the existing physical and chemical conditions. The oxide films are useless unless they can be automatically kept in repair, for they are subject to wear.

From the discussion under the section "Theory of Corrosion with Fatty Acids," it was seen that the composition of the scale was not determined. However, some of the properties of the scales were observed, and these help to give an explanation of the corrosion rates. Where the scales were loosely attached, flaky, and soft, the corrosion rates were high. In these cases, the films that were formed must have allowed the corrosive acids to diffuse to the surface of the retal and cause considerable corrosion.

effect of chromium content on the corrosion Rates. - Curve 2 shows the effect of chromium content on the corrosion rates by hot fatty acids. It can be seen from this curve that as the chromium content is increased, the corrosion rate decreases markedly to a composition of about 24 per cent Cr where the curve flattens off. However, even in the case of the 24 per cent Cr there is too much corrosion to warrant its use for the fabrication of equipment for the distillation of the crude tallol. In these cases the film was soft and porous so that it did not give adequate protection to any of the alloys. The surfaces appeared pitted in addition to the etching effect, and this was further cause for discarding the alloy for possible use.

Effect of Chromium-Nickel Content on Corrosion Rates. - Previous tests (23) (29) have shown that the addition of nickel to chromium steels increased their resistance until the addition of 8 per cent Ni with 18 per cent Cr produced a steel which showed border line resistance, for in some cases it has good resistance while in other cases it exhibits only a fair corrosion

GRAPH 2



resistance. Of the 18-8 alloys that were tested in these tests, most of them showed only fair resistance to corrosion. However, as the alloying elements are increased above this composition, there is a charge in which a series of highly resistant alloys are formed. The 25 per cent Cr and 13 per cent Ni alloys showed the best resistance of all the chrome-nickel alloys that were tested, for they lost little or no weight during the corrosion tests. The 25 per cent Ni and 20 per cent Cr alloy did not show as good resistance as the 25-13 chrome-nickel steel, but it was highly resistant to the corrosive effects. From this it can be seen that increasing the amount of nickel above about 13 per cent does not increase the corrosion resistance to any appreciable extent.

Effect of Method of Fabrication. - The form in which the metal is fabricated seemed to have some effect upon the corresponding relied alloys with the same composition. An explanation of this effect may be postulated from the appearance of the surface. Since the surface in the case of the cast alloys was relatively rough, the protective film that was formed may have been discontinuous in nature and allowed some corresion to take place, and in addition the cast surface has a larger surface of contact to the fatty acids.

The cast, high nickel chrome alloy of 66 per cent Ni and 20 per cent Cr did not show very good resistance. The cast 38 per cent Ni, 18 per cent Cr alloy showed somewhat better resistance. From this and the previous discussion, it seems that neither the very low all yed nor the extremely high alloyed chrome-nickel alloys show the best resistance, but intermediate

alleys have the best corrosion resistance properties.

Effect of Molybdenum on the Corrosion Resistance of 18-8 Steels.
The 18-8 steels alloyed with 3 to 4 per cent molybdenum exhibited a corresion resistance equal to that of the 25 per cent Cr, 13 per cent Ni alloys. Hence, it seems unnecessary to use the highly alloyed chromenickel steels if a small amount of molybdenum is added to the common 18-8 variety. The molybdenum gives the 18-8 steels greater resistance against intergranular attack.

Effect of Silicon on Corrosion Resistance. - The cast alloys of iron and 14 per cent silicon, tested in run 1, showed no loss in weight. This effect is obtained due to the presence of the very corrosion resistant iron silicide in the all y.

Corrosion Resistance of Nickel and its Alloys. - The only alloy of nickel that showed resistance comparable with that of the molybdenum steels was an alloy of 80 per cent Ni and 20 per cent Cr. The alloy of 50 per cent Ni, 18 per cent Cr, 20 per cent No, and 6 per cent N, which was the next best resistant nickel alloy had only a resistance comparable with that of a plain 18-8 steel. Pure nickel had an intermediate resistance in respect to the nickel alloys with an alloy of 67 per cent Ni and 30 per cent Cu of only fair resistance. The east iron containing about 20 per cent Ni, 2 per cent Cr with and without 7 per cent Cu showed very poor corrosion resistance to the hot fatty acids.

Most of the nickel alloys were coated with a very loose scale that was easily washed off. Since this protective film was soft and non-adherent, the nickel alloys would not be expected to have a very high

corresion resistance. The more resistant alloys did not show this scaling or pitting effect.

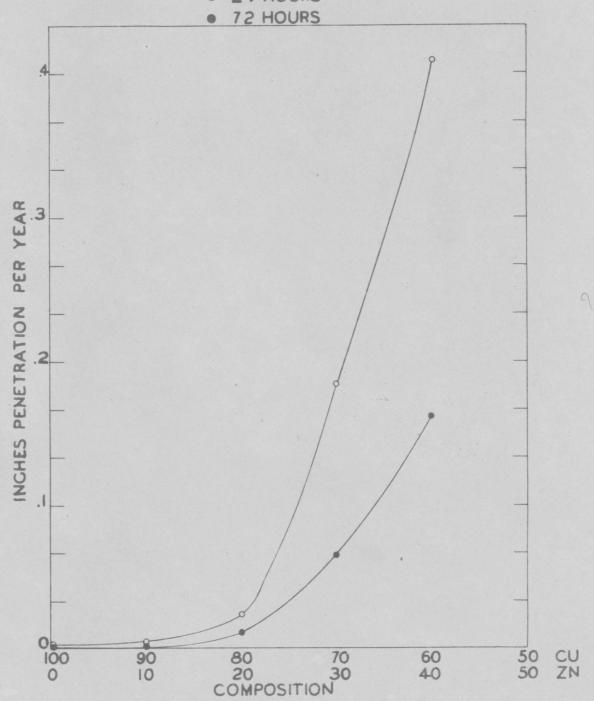
Corrosion Resistance of Aluminum and its Alloys. The cast aluminum alloys containing 4 per cent Cu or 12 per cent Si showed slight gain in weight which may have been due to the formation of a film. The alloys containing 5 per cent Si, 0.25 per cent Cr, and 1.3 and 2.5 per cent Mg had corrosion rates about the same magnitude as aluminum. The pure aluminum exhibited a corrosion resistance similar to that of 13-8 chromenickel steel.

characteristic of copper and its alloys was the very noticeable scaling and pitting effects that were the result of corrosion. Pure copper showed better resistance than any of its alloys that were tested. The alloying effect, shown by varying the amount of zinc added in submation with the copper, may be cited as an example of this effect as shown in curve 1. This curve shows the effect of increasing the amount of zinc in brasses on their corrosion resistance. The curve is plotted as percentage composition against corrosion rates for both the 24 hour and 72 hour tests. In examining the curve, it is noticed that there is a break in the curve at about 80 per cent Cu and 20 per cent 2n which may be due to the formation of a less resistant solid solution. The alloys of copper and about 10 per cent aluminum did not show very good corrosion resistance. The tin bronzes showed intermediate resistance while alloying with about 3 per cent silicon gave inconsistent results.

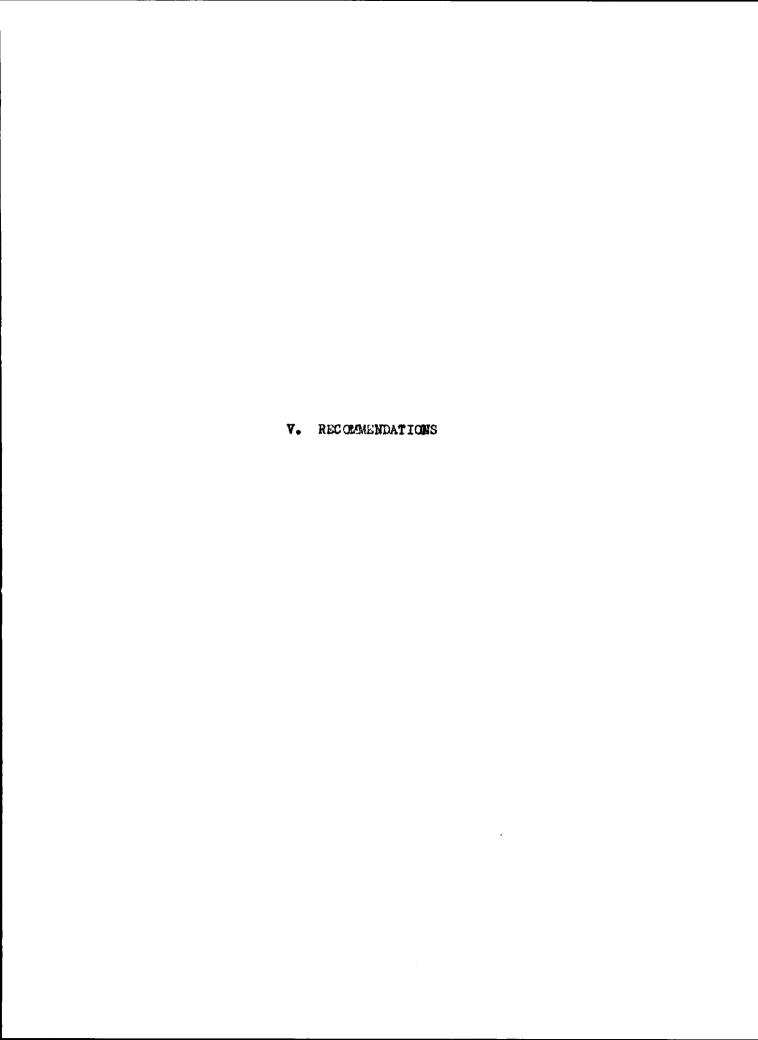
GRAPH 1

CORROSION RATE OF COPPER-ZINC ALLOYS IN CRUDE FATTY ACIDS TEMPERATURE 300 C

0 24 HOURS



Checking of Results. Check samples were not run in most cases, and hence the results of further tests may change the relative positions of the alloys slightly, for there is relatively little difference in corrosion rates in many cases. However, the magnitude of the corrosion rates will not be materially changed.



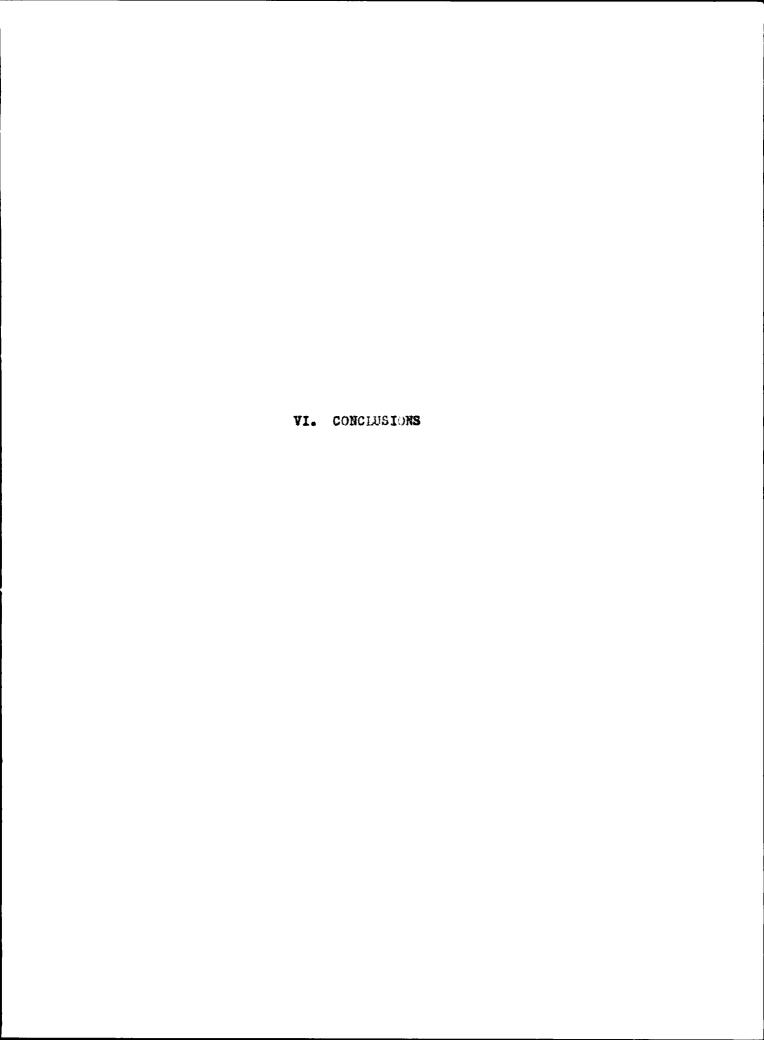
V. RECOMMENDATIONS

After completion of these corrosion tests there were many questions which remained unsettled that suggest the advisability of further research. With the results of this thesis in mind, the following recommendations are made:

- l. In order to obtain the true corrosion effects of plant conditions, it seems advisable to test the alloys which have been found suitable for materials of construction in actual plant distillations.
- 2. Since the mode of distillation in practice gives the fatty acids a high velocity, it would be of interest to subject the alloys to the effects of high velocity.
- 3. The effect of heat transfer on the corrodibility of the alloys should be tested, for this factor may have considerable effect on the corrosion rate.
- 4. Since the alloys may have an entirely different rate of corrosion with the wapors of the fatty acids, the various alloys should be tested with respect to their corrosive effect.
- 5. Since it is known that some cold working has deleterious effects on corrosion rate, it would be important to test many samples of the same metal that have been subjected to different treatments.
- G. The finish on a metal often affects the rate of corrosion, and it would be interesting to know the initial and final effects of the surfact

condition on the rate of corrosion.

- 7. The steel and nickel alloys should be tested in the Incomel kettle to determine its effect on their corrosion rates.
- 8. If it is possible to get more alloys with a wider variation in alloying elements, the effects of the alloying element could be determined more quantatively.
- 9. Since the mechanism of corrosion in the fatty acids is not definitely known, this problem presents an interesting subject for research. In order to accomplish this, the following problems would have to be solved:
- A. The possibility of ionization at high temporatures should be investigated.
- B. The question of the possible oxidizing properties of the fatty acids should be investigated.
- C. The composition of the films should be investigated to determine the products of the corresion reaction.
- D. The conductivity of the hot solution should be measured to determine the possibility of deposition of one metal upon another.
- E. The possibility of corrosive sulfur compounds present in the tallol should be investigated.
- 10. If some method could be obtained of dissolving the films from the metals after corrosion, a better and more accurate measure of the corrosion rate could be obtained.
- 11. Check samples should be run on each alloy in order to get a more accurate measure of the relative corrosion rates.



VI. CONCLUSIONS

From the results obtained, the following conclusions have been drawn:

- 1. The material that is recommended for the fabrication of still tubes is the 25 per cent Cr and 13 per cent Ni steel which showed no attack after seventy-two hours exposure to the hot fatty acids.
- 2. The 18-8-3 chroms-nickel-molybdenum steel which showed a maximum corrosion of .0002 inches penetration per year can not be recommended because it is not available in the form of seamless tubing.
- 3. The 18-8 chrome-nickel steels showed considerable variation in corrosion resistance, but none had more than a fair resistance.
- 4. The chrome-nickel alloys with 10-20 per cent or and 30-67 per cent Ni showed only a resistance comparable with the 18-3 chrome-nickel alloys.
- 5. The cast alloy of 25 per cent or and 13 per cent Ni and the 18-8-3 chrome-nickel-molybdenum showed considerably less resistance than the rolled loys of the same composition.
- 6. The chrome steels showed very high corrosion rates, but the rates decreased as the percentage of chromium increased.
- 7. The cast alloy of iron and 14 per cent Si showed no corrosive effect from the hot acids.
 - 8. The 20 per cent Cr and 30 per cent N1 alloy exhibited the best

resistance of the nickel alloys, with pure nickel exhibiting only an intermediate resistance. The alloy of 67 per cent Ni and 30 per cent Cu showed only a fair resistance to the hot fatty acids.

- 9. The cast alloys with about 4 per cent Cu or 12 per cent Si showed a slight gain in weight after exposure to the hot, fatty acids.
- 10. The addition of 5 per cent Si, .25 per cent Cr, or 2.5 per cent Mc did not exhibit very much difference in corrosion rate from the rate of pure aluminum. The pure aluminum had a corrosion rate of the same magnitude as 18-8 chrome-nickel steel.
- 11. Pure copper gave a greater resistance than any of its alloys that were tested. In the brasses, as the percentage of zinc increased the corrosion rate increased very rapidly. At a composition of about 30 per cent Cu and 20 per cent Zn, the rate of corrosion showed a very abrupt increase.
- 12. The alloying of copper with about 2.6 per cent Si, 4-7 per cent Sn or 7-10 per cent Al gave high corrosion rates in all cases, with the silicon alloys having a somewhat better resistance than the Sn and Al alloys of copper.
- 13. Scaling was noticeable in the chrome steels in the form of a soft, porous, black scale. The more resistant steels showed no sign of either scaling or pitting.

All nickel alloys except the ones of highest resistance were covered with a loose, flaky, bluish colored scale after exposure to the fatty acids.

All the copper alloys showed a somewhat more adherent blue-gray scale than the nickel alloys.

None of the aluminum alloys showed signs of scaling.

14. The less resistant steels, nickel alloys, and most copper alloys

had signs of pitting.

- 15. From twenty-four hour tests, 18-8 chrome-nickel steels showed a corrosion rate 75 per cent less in the second twenty-four hours using fresh samples of the alloy in each test. In the same manner a 15 per cent chrome steel showed a corrosion rate 25 per cent less than in the first twenty-four hour test.
- 16. From tests of nickel alloys in both stainless steel and Inconel kettles, it was found that the composition of the kettle had little effect either on the rate of corrosion or the relative positions of the alloys with one another.
- 17. Since the acid number decreased from about 150 to 90 in the first twenty-four hours of the test and to about 60 in seventy-two hours, the results of these tests can only be considered as relative results, and not as a quantative measure of the corrosion rate that would be obtained in the plant.
- 18. The welding of chrome-nickel alloys does not produce a higher corrosion rate than the metal from which the welds are made provided that they are properly annealed.
- 19. Since check samples were not run in most cases, the relative positions of one alloy with another may vary somewhat on further tests, for there is relatively little difference in corrosion rates in many cases.

VII. SUMMARY

VII. SUMMARY

This investigation was undertaken in order to determine the effect of alloying on the corrodibility of various alloys to hot crude tallol. To accomplish this, a series of eighty-five iron, nickel, copper, and aluminum alloys were exposed to twenty-four and seventy-two hour corrosion tests to the crude fatty acids. The tests were carried out in stainless steel and Incomel bettles that were thermostatically controlled at 300° C.

The 25 per cent Cr and 13 per cent Ni and the 18-8 chromonickel alloy with 3-4 per cent No exhibited the best corrosion resistance to the crude hot tallol. The 18-8 chrome-nickel and the high nickel-chrome alloys had only a fair resistance while the plain chrome alloys had high corrosion rates.

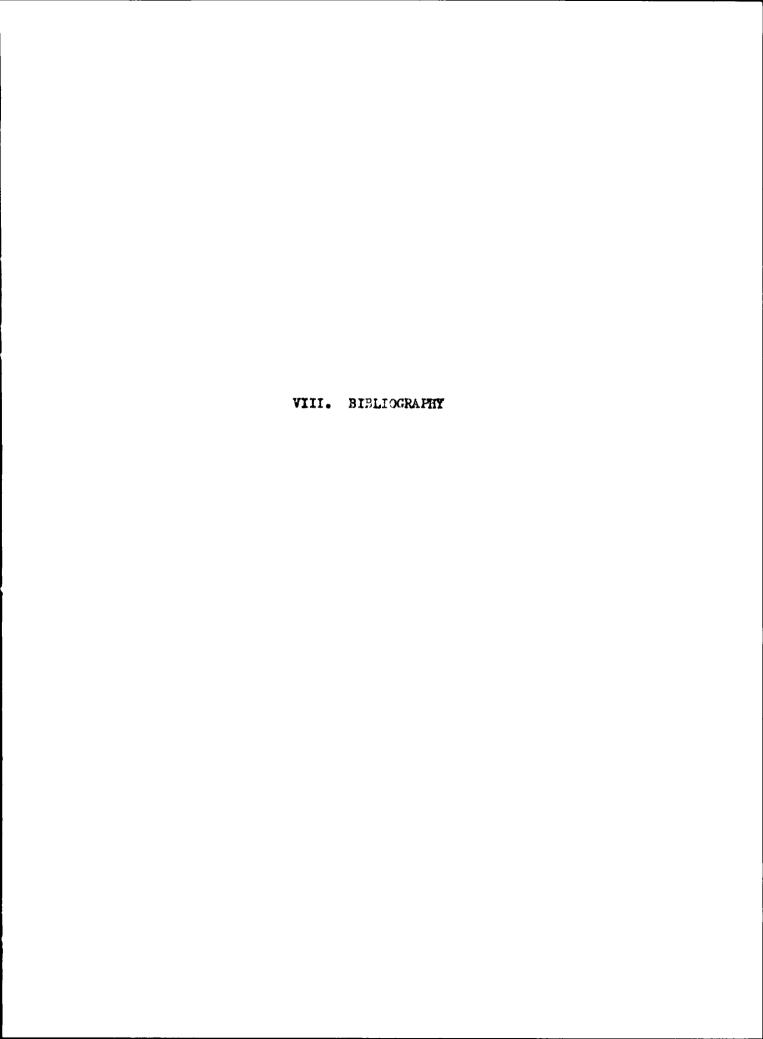
Pure copper exhibited a better resistance to the corrosive effects than any of its alloys, but all the alloys scaled very badly.

The 80 per cent Ni and 20 per cent Cr alloy were attacked very little, but pure nickel and most of the other nickel alloys were attacked fairly rapidly and were scaled considerably.

Only the cast alloy of aluminum containing 4 per cent Cu exhibited good resistance qualities while other alloying elements did not affect the rate of corrosion of pure aluminum appreciably even though no scaling was noticeable.

The acid number had considerable affect on the corrosion rates while the composition of the kettle had little or no effect on the corrosion rate.

Filing of the samples instigated pitting in the file marks while machining did not appreciably affect the corrosion rates.



VIII. BIBLIOGRAPHY

- Anonymous Preventing Corrosion of Metal Surfaces.
 German Patent 559,893, July 17, 1927. Original not seem.
 Chem. Abst. 27, 700 (1933)
- 2. Baerlecken, E. The Resistance of Metallic Materials toward Corrosion by Hot Fatty Acids. Fette and Seifen 44, 228-9 (1937)
- S. Bain, E. C. Some Fundamental Characteristics of Stainless Steels.
 Jour. Soc. Chem. Ind. 51, 662-7 (1932)
- 4. Cox, G. L. Corrosion of Metals in the Scap and Allied Industries.

 Ind. and Eng. Chem. 30, 1256 (1938)
- 5. de Keghel, H. Composition and Uses of Tallol.

 Rev. Chem. Ind. 35, 170-3 (1926) Original not seen. Chem.

 Abst. 21, 1354 (1927)
- 6. ibid. F. 202-8
- 7. Dittmer, M. Tall Oil, a Product of Sulfate Pulp Man'f'ture.

 Z. angew. Chem. 39, 262-9 (1026) Original not seen.

 Chem. Abst. 20, 2072 (1926)
- 8. Evans, U. R. The Fassivity of Metals.

 Jour. Chem. Soc. 47, 55, 62, 73, (1928)
- 9. Hatfield, W. H. Heat Resistant and Acid Resistant Steels.

Trans. of Chem. Engr. Congress of World Power Congress
1, 42 (1936)

- 10. Hedges, E. S. "Protective Films on Metals."

 D. Van Hostrand Co. (1933)
- 11. Heyer, G. O. Corrosion of Lead by Fatty Acids in the Presence of Iron. Seifensider Ztg. 60, 131-2, 165-7 (1933) Original not seen. Chem. Abst. 27, 2592 (1933)
- 12. Hubscher, J. Swedish Rosin Oil
 Seifensider Ttg. 48, 231 (1921) Original not seen. Chem.
 Ebst. 15, 2177 (1921)
- 13. Johnston, J. Corrosion Problems.
 Ind. end Eng. Chem. 26, 1238 (1934)
- 14. Killeffer, D. H. Paper Goes South.

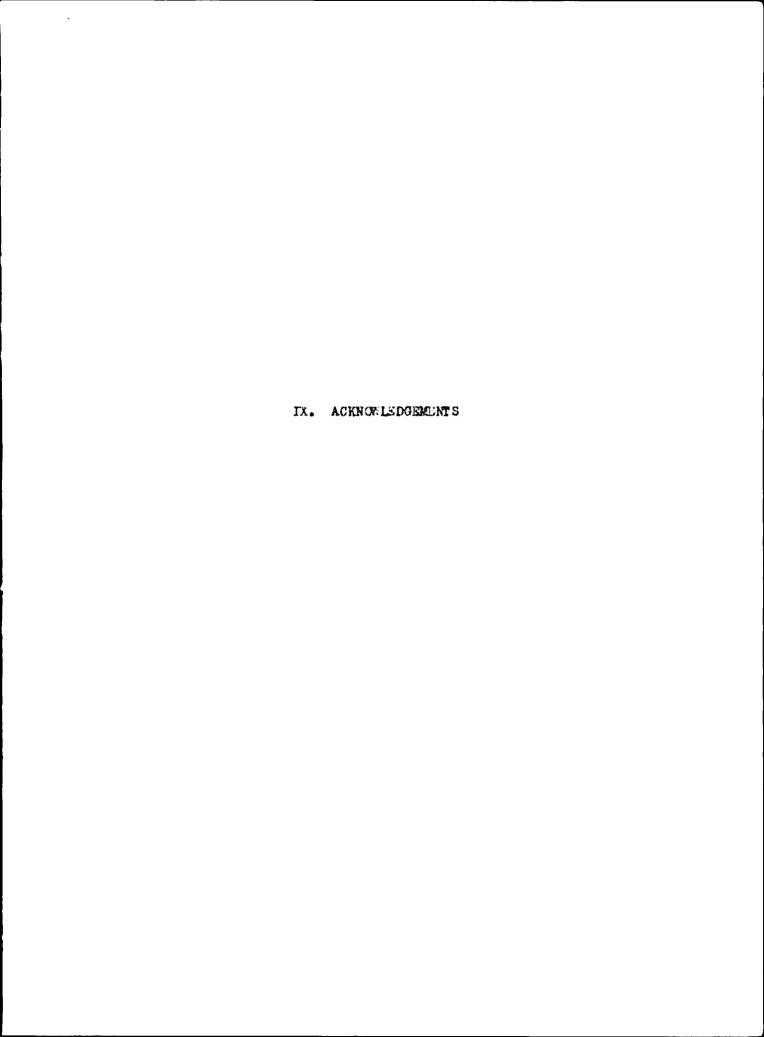
 Ind. and Eng. Chem. 50 1110 (1958)
- 15. Kino, K. Corrosion Tests of Some Metals and Alloys by a Higher Fatty Acid at 350-340°. Jour. Soc. Chem. Ind. (Japan)
 40, 312 (1937) Original not seen. Chem. Abst. 32, 99 (1938)
- 16. ibid. P. 464
- 17. Lee, J. A. Netals and Alloys Used in the Construction of Chem.

 Plants. Trans. of Chem. Engr. Congress of the World Power Congress

 1, 469 (1936)
- 18. Maxwell, H. L. Stainless Steels for Use in Chemical Equipment.

 Trans. of Amer. Instit. of Chem. Engrs. 35, 167 (1959)
- 19. McKay, R. J. and Worthington, R., "Corrosion Resistance of Metals and Alloys." Reinhold Pub. Corp. (1936)

- 20. Ferry, J. H. "Chemical Engineers Handbook." P. 1725
 McGraw-Hill Book Co. (1934)
- 21. Speller, E. N. "Corrosion, Causes and Prevention; An Engineering Problem." McGraw-Hill Book Co. P. 613 (1935)
- 22. ibid. F. 98-100
- 23. Tinder, E. K. Corrosion of Alloys by Crude Fatty Acids
 Unpublished Thesis, Library, V.P.I., Blacksburg, Va. (1938)
- 24. Vilbrandt, F. C. and Ward, L. E. Corrosion Characteristics in Distillation of Fatty Acids. Trans. Electro. Soc. 73, 13 (1938)
- 25. Ward, L. E. Design Characteristics For By-Product Fatty Acids
 Recovery. Unpublished Thesis, Library, V.P.I., Blacksburg, Va.
 P. 3 (1938)
- 26. ibid. P. 3
- 27. ibid. P. 58
- 28. ibid. P. 71
- 29. ibid. P. 86
- 30. Watts, O. P. The Corrosion of Metals. Univ. of Wis. Eng. Exp. Sta. Bull. 80 , (1938)



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