File in Rx Chem "Materials of Construction"

DOW CHEMICAL U.S.A.

February 12, 1988

LOUISIANA DIVISION
P. O. BOX 150
PLAQUEMINE, LOUISIANA 70765-0150
504 389-8000

P. J. Bilello, B-3601
C. W. Brannan, B-2601

cc: W. T. Austin, B-3701
H. M. Bell, B-4701
J. Y. Pennington, B-2510

PASSIVATION OF TITANIUM IN CHLORINE

The attached article is the culmination of a literature search by Rich Chauviere of the Chlor-Alkali Tech Center. Nothing completely new here, but an excellent summary.

Conclusions:

1. As the temperature of chlorine increases, more water is required for passivation. About 1.5% water is required around 400 degrees F. I have not seen any data at higher temperatures.

2. Flowing conditions require less water for passivation than static conditions.

3. Surface condition of the titanium has an effect - a rough or scratched surface is more likely to react than a smooth one.

4. Pressure is thought to have an effect, but this article did not address that variable.

5. You will notice that the data is somewhat erratic, i.e., not all the specimens reacted at a given set of conditions.

6. It is pointed out that once a reaction begins it is self sustaining, regardless of water content in the chlorine, unless there is a film of water on the metal.

In short, it must be recognized that the water content in chlorine required to prevent a reaction with titanium is not a constant. Utilize this article for planning safely.

R. W. Cochran
Safety/Loss Prevention/Security

Enc.

am

DO 073035
CONFIDENTIAL

Factors Affecting Water Content Needed to Passivate Titanium in Chlorine*

By E.E.MILLAWAY and M.H. KLEINMAN*

ABSTRACT

Titanium generally is reactive to dry, gaseous chlorine. A small amount of water in gaseous chlorine will inhibit this reaction. A testing program showed the amount of water required for inhibition varied with exposure conditions from about 0.20 to 1.1 over the range of about 25 to 175 C (77-347 F). When water content in the gaseous chlorine is sufficient titanium can be considered passive.

Data were obtained mostly by scratching to expose fresh titanium surfaces to gaseous chlorine and observing reactions. Under some conditions a definite reaction sequence often took place, which could be observed from initiation to ignition of a specimen. Some data were obtained from exposure of undisturbed titanium specimens in gaseous chlorine.

The water content required to passivate titanium in chlorine gas was found to be dependent upon temperature, gas flow rate and chlorine pressure. It was affected also by titanium surface condition, some roughened surfaces showing increased reactivity. Under static conditions involving chlorine of high purity, water required was greater than under flow conditions in dried, crude Hooker cell chlorine. Undisturbed titanium surfaces exposed at 195 C (382 F) for over a year showed no reaction when chlorine water content was 1.5 percent or more.

INTRODUCTION

Titanium is known to react in dry chlorine but to be passive in wet chlorine. Titanium specimens ignited and burned[1] after 139 days in 97 percent chlorine, balance carbon dioxide, hydrogen, air, etc., 0.0005 percent water at normal temperature.

In a 99-day test in saturated chlorine in a cell header evaporator space at 206.6 F (97 C) the average corrosion rate of titanium was 0.0003-in per year.[1]

The amount of water required to stop the attack by chlorine on titanium has been reported as 0.005 percent,[2] as 0.1 percent[3] and 0.35 percent. The 0.35 percent was obtained by scratching a titanium surface in an atmosphere of chlorine.[4] This investigation was made to develop more information on the amount of water necessary to inhibit the reaction of titanium with chlorine.

Because some prior testing had shown erratic results when titanium was exposed to an atmosphere of chlorine, static exposure of titanium was not used as a primary test method. Instead, scratching the surface to expose fresh titanium to the chlorine was preferred. Static exposure tests, however, were used in an attempt to verify some of the data obtained by exposing a fresh titanium surface to chlorine. Some work was done also to find a more reliable test method than the ones used previously.

One series of tests was made with relatively high purity bottled chlorine; another was made with dried, crude Hooker cell chlorine so results would be more consistent with industrial plant exposure conditions.

EXPERIMENTAL PROCEDURES

Static Tests

Static exposure tests were made by placing titanium specimens in gaseous chlorine of various water contents at several temperatures for extended periods. The exposure tubes used are shown in Figure 1. Test specimens were 1/4 x 1 1/2 x 0.035-in sheet of ASTM 265-57T Grade 2. Specimens were cut, stamped with an identification number, scrubbed in hot water with an abrasive cleaner, rinsed, pickled for about one minute in a 10.5 HNO_3-1.5 HF (vol.%) solution, rinsed in distilled water, dried and weighed. During assembly, specimens were placed in one end of the glass tubes and cooled with flowing helium until the opposite end was sealed. Then the tubes were evacuated, a Cl_2-H_2O mixture added and the stems sealed off. Quantities of $Cl_2 + H_2O$ were such as to give just slightly above atmospheric pressure at the exposure temperatures. For high water content tests the required water was added by volume measurement with a 50-microliter Hamilton[(1)] syringe, frozen with dry ice and acetone, the tubes evacuated, then warmed slightly, and dry Cl_2 admitted and the stems sealed off. The tubes were placed in ovens at the desired temperatures and inspected periodically.

Non-Flow Scratch Tests

For making tests of fresh titanium surfaces exposed to non-flowing chlorine the apparatus shown schematically in Figure 2 was used. A

* A paper presented at the 22nd Conference, National Association of Corrosion Engineers, Miami Beach, Florida, April 15-22, 1966.

Titanium Metals Corp. of America, Henderson, Nevada.

(1) Hamilton Co., P. O. Box 307, Whittier, California.

...ched amount of water could be added to a ...wn volume of dry chlorine to obtain a known ...ter content. Details of the specimen exposure ... are shown schematically in Figure 3. Higher ...peratures were obtained by wrapping the ...imen exposure tube with heating tape. For ... non-flow scratch and static tests commercial ...ried chlorine of 99.5 percent purity was used. ...ecimens used in non-flow scratch tests were ... x 3 x 0.035-in sheet of ASTM 265-52T Grade 2 ... a 1/8-in diameter hole drilled near one ... They were scrubbed in hot water with an ...rasive cleaner, rinsed in both tap and dis...led water, air dried and stored in a covered ...ass container until used.

...fter a specimen was placed in the holder ... the exposure tube, the tube was assembled ... evacuated to a few microns and the chlorine-...ter mixture introduced into it. The specimen ... then scratched and observed for reaction. ... no reaction occurred in about 5 minutes the ...ecimen was scratched again. This was repeated ... about an hour.

...low Scratch Tests

The apparatus shown schematically in Figure 4 ... used for tests under flowing conditions. Water ... introduced by mixing streams of nearly-...turated and of dry, crude Hooker cell chlorine ... then computing the water content of the ... ...ture, assuming saturation of the stream that ... passed through water. For most flowing ... dried, crude Hooker cell chlorine that had ... been compressed and revaporized was used.

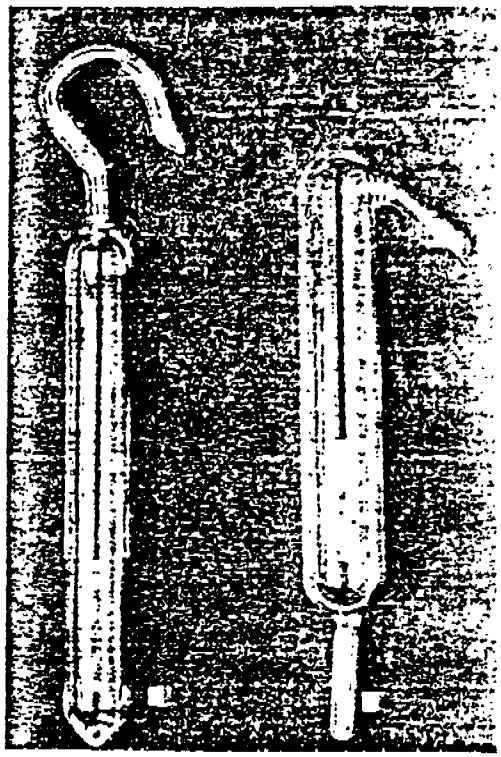


Figure 1 - A. Sealed tubes for low water content chlorine testing of titanium. 0. to 0.93 percent H_2O. B. Sealed tubes for high water content chlorine testing of titanium. 1.5 to 6.9 percent H_2O.

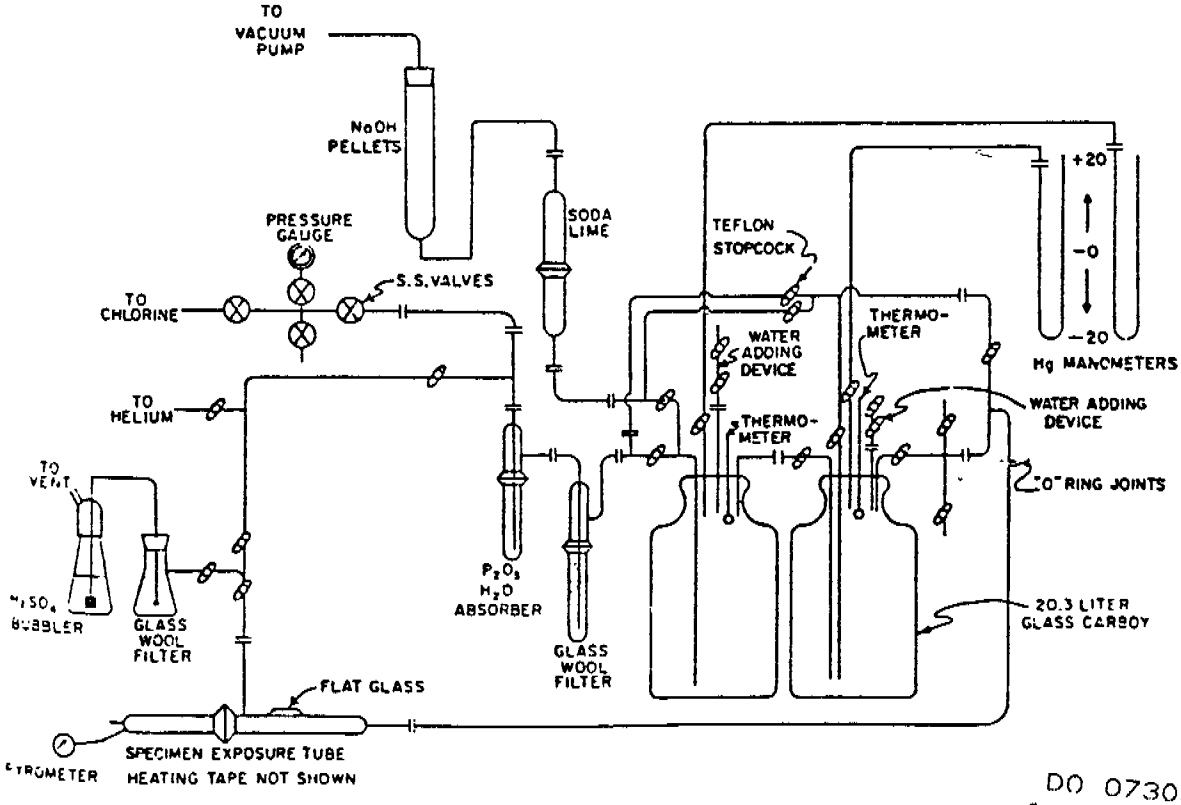


Figure 2 - Chlorine test apparatus.

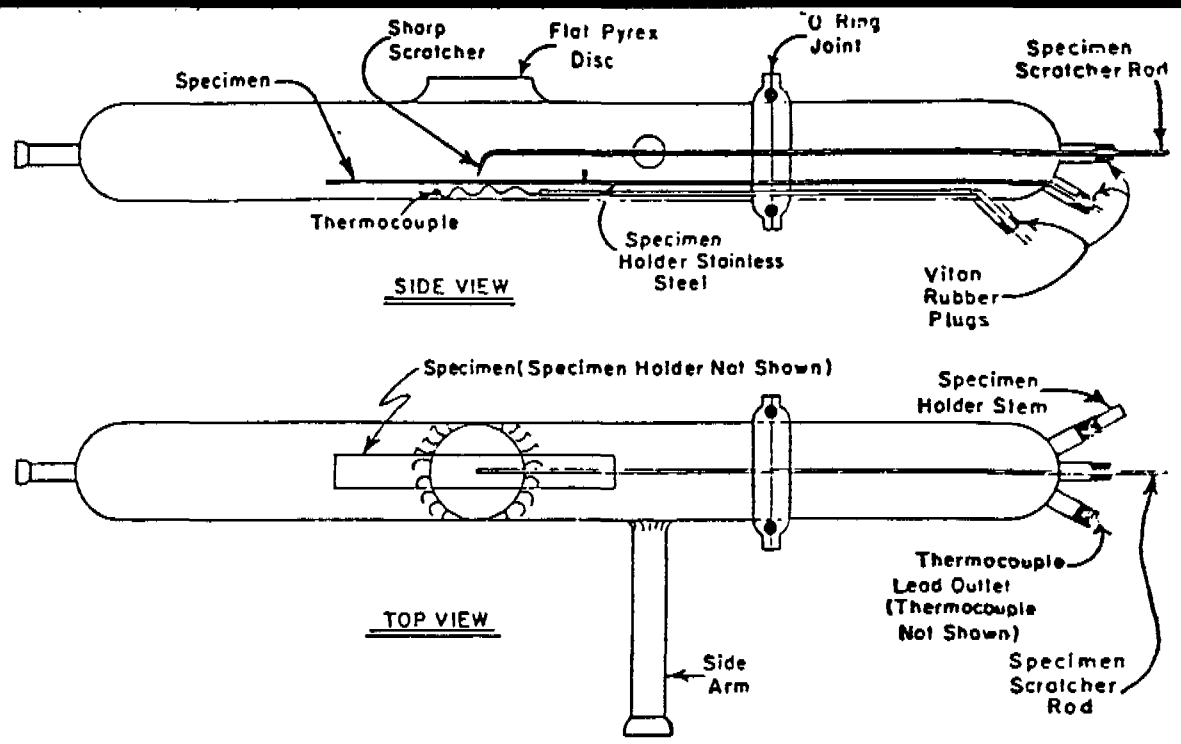


Figure 3 – Specimen exposure tube of 25mm heat resistant glass tubing and specimen handling arrangement. Heating tape not shown.

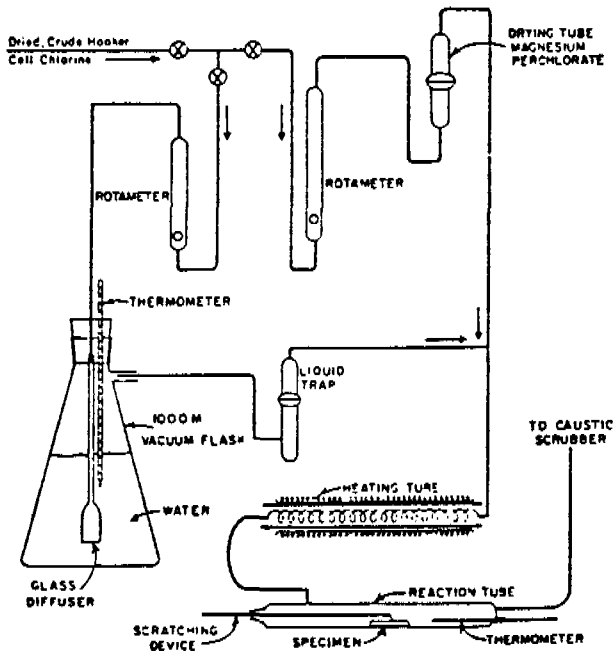


Figure 4 – Setup used for flowing chlorine studies.

Specimens used in these scratching tests were 3/8 x 3 x 0.025-in sheets of ASTM 265-52T Grade 4. Preparation was the same as for other scratch tests.

Specimens of unalloyed titanium were put into the exposure tubes and when the desired conditions were reached the surface was scratched to expose fresh titanium. The scratched surface was observed for reactions for periods va from a few seconds to 10 minutes. If no re occurred, the surface was scratched again process was repeated for periods from 5 m to 4 hours until it appeared certain that a re was not going to take place. A reactior considered to take place when any visible st change occurred.

Most of the scratching was done with a shar Ti-6Al-4V alloy rod. Some scratching was with a sharpened stainless steel rod, a p glass rod or a diamond-tipped device.

Unless otherwise noted, the tests were at close to atmospheric pressure. The che composition of ASTM Designation B265-52T g are given in Table 1.

Table 1 – Chemical Composition, Percent[1]

Element	Grade Number 1	2	3	
Titanium, min.	99.3	99.2	99.0	98.
Nitrogen, max.	0.08	0.10	0.15	0.
Carbon, max.	0.05	0.20	0.20	0.
Iron, max.	0.12	0.25	0.25	0.
Tungsten, max.	0.08	0.02	0.02	0.
Oxygen, max.	0.15	0.20	0.25	0.

[1] Chromium, magnesium, aluminum, mangan nickel, copper, lead, molybdenum, vanad and other elements not specifically mentic shall not total over 0.25 percent and no element not specifically mentioned shall exc 0.10 percent.

RESULTS

Static Tests

Results of static exposures are shown in Figure 5. Detailed results are tabulated in Table 2.

No reactions occurred in 17 months' static exposure tests when titanium was exposed to chlorine that contained 0.71 and 0.93 percent water at room temperature. The chlorine to which 0.93 percent water had been added was probably supersaturated some of the time.

In Figure 5 are shown percentages of specimens in groups of five that had reacted after 17 months' exposure to chlorine with several levels of water content and at four temperatures. It should be noted that reactions did not occur at 50 C (122 F) or in dry chlorine at 135 C (275 F) while reactions did occur at room temperature. One reason for this is that specimens were placed in their specific chlorine atmospheres before ovens were available and were thus exposed at room temperature prior to the higher temperature exposure. Thus specimens that had a tendency to react did so at room temperature. At temperatures of about 195 C (383 F), 0.93 percent water was insufficient for passivation.

Groups of five specimens each tested at 195 C with higher water contents of 1.5, 2.9, 4.3, 5.6 and 6.5 percent showed no reactions after 21 months' exposure. Some temperatures in Figure 5 are five degrees below oven settings and were so plotted because of temperature variations.

Table 2 - Specimens Exposed to Chlorine in Sealed Tubes and Number of Reactions that Occurred in 17 Months

Chlorine Water Content %	NUMBER OF SPECIMENS						
	Used	Reacting on Loading	Placed at 190-200 C	Reacting at 190-200 C	Placed at 130-140 C	Reacting at 130-140 C	Placed at 100-110 C
nil	26	3[1]	5	5[5]	5	0	5
0.12	18	1[2]	1	1[6]	0	0	5
0.14	9	0	4	4[7]	5	5[12]	0
0.24	25	4[3]	5	5[8]	5	5[13]	5
0.46	23	3[4]	6	6[9]	5	3[14]	4
0.71	24	0	5	5[10]	5	2[18]	5
0.93 (sat.)	24	0	5	5[11]	5	0	5

Chlorine Water Content %	NUMBER OF SPECIMENS					
	Reacting at 100-110 C	Placed at 50-55 C	Reacting at 50-55 C	Left at Room Temp.	Reacting at Room Temp. Test	Reacting at Room Temp. Total[19]
nil	*[15]	5	0	3	1[17]	4
0.12	*[15]	5	0	5	1[20]	2
0.14	0	0	0	0	0	-
0.24	*[15]	5	0	1	0	4
0.46	*[16]	5	0	0	0	3
0.71	*[15]	5	0	4	0	0
0.93 (sat.)	*[15]	5	0	4	0	0

*Specimens lost when oven temperature inadvertently was raised to approximately 250 C.
** By loading is meant placing titanium specimens and chlorine gas in tubes.

(1) Reacted approximately 1 minute to 30 minutes after loading.**
(2) Reacted about 5 minutes after loading.
(3) Reacted in about 1 minute to 1 day after loading.
(4) Reacted 5 days after loading.
(5) Reacted in from 1 week to 2 months.
(6) Reacted in 4 hours.
(7) Reacted in from 1 day to 2 months.
(8) Reacted in from 1 day to 2 months.
(9) Reacted in from 1 week to 2 months
(10) Reacted in from 1 to 9 days.
(11) All reacted in 2 months when containers taken from oven and examined.
(12) All reacted in 2 months ± 1 week.
(13) Reacted in from 1 to 3 months
(14) Reacted in from 2 to 5 months.
(15) Specimens lost about 3 1/2 months after placing in 105-110 C oven when temperature inadvertently raised to approximately 250 C.
(16) One specimen survived the 250 C in the 105-110 C oven and was placed in 190-200 C oven where it reacted approximately 1 month later.
(17) Specimen reacted between 4th and 5th month. Slow reaction.
(18) Specimen reacted 5 1/2 months after placing in oven.
(19) Specimens tested plus those that reacted on loading.
(20) Found reacted after 17 months.

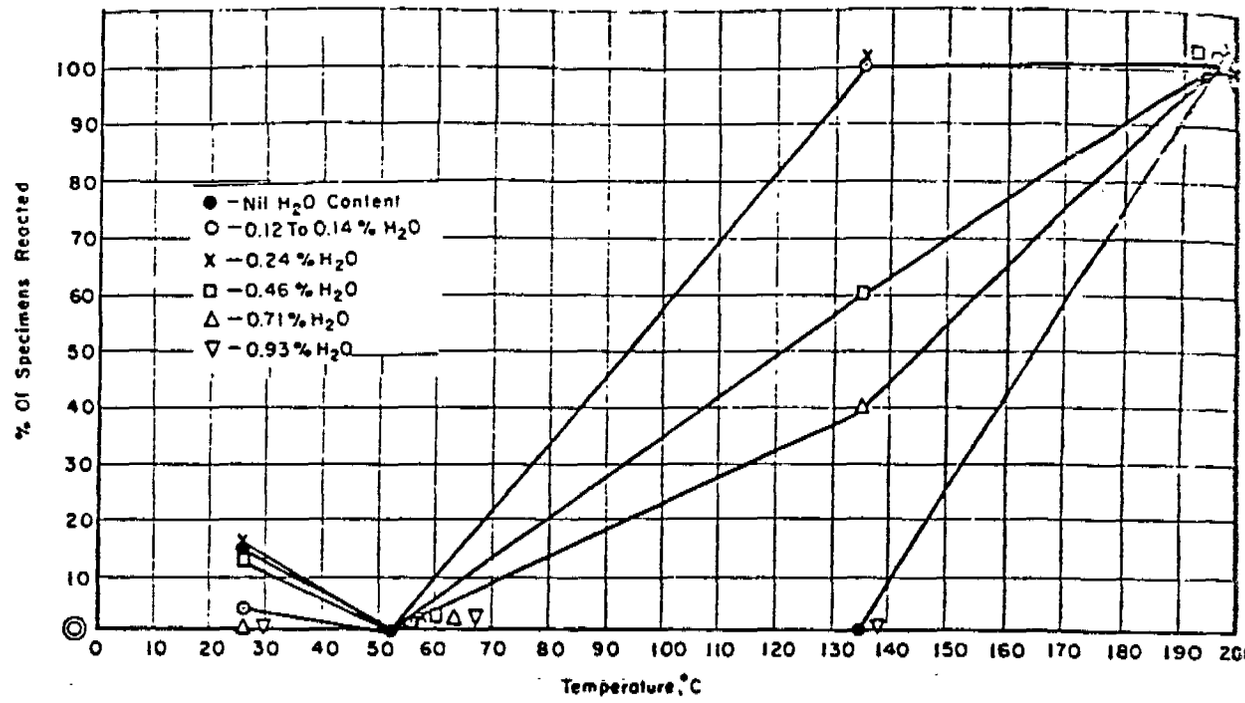


Figure 5 – Results of static tests of unalloyed titanium exposed to Cl_2 gas at varying water contents and varying temperatures.

Non-Flow Scratch Tests

Summarized results of scratching tests made under non-flow conditions using bottled chlorine are shown in Table 3. In these tests reactions were obtained in chlorine that contained about 0.85 percent water, near saturation at 26 C (79 F). When less than 0.85 percent water was present, reactions occurred readily with scratching on all but a vacuum annealed specimen and when the chlorine pressure was 16-in of Hg or less. No reaction occurred when liquid water was added to the reactor tube to assure saturation.

Table 3 – Results of Tests of Unalloyed Titanium Sheet Scratched in Bottled Chlorine

Test No.	% H_2O	Test C	Test Type	Pressure	No. Tests	Results
1	Dry	27	Non-Flow	Atm.	1	Color appeared after 23 min. of gentle scratching. Specimen ignited after 31 min.
2	Dry	26	"	Atm.	1	No reaction when scratched.
2(1)	Dry	92(2)	"	Atm.	1	When temp. raised to 92° reaction started.
3	.27	26	"	Atm.	1	Reaction started after 10 min.
4	.59	26	"	Atm.	1	Color started in 13 min.
5	.80	26	"	Atm.	2	Reacted after 1 and 47 min.
6	Abt . 85(3)	26	"	Atm.	4	Three reacted. One did not.
7	Dry	26	"	14"	1	No reaction after scratching.
7	Dry	26	"	Raised to 20" Hg	3(6)	Reacted.
8	Dry	26	"	16" Hg	1	No reaction.
8	Dry	26	"	To 18" Hg		Reacted after 12 min.
9	Dry	26	"	20"	1	No reaction.
10	Dry	26	"	22"	1	Reacted 14 min. after scratching.
11	Dry	26	"	3-4 psig	2	Light scratching caused immediate reaction.
12(3)	Abt. 85(3)	26	Flow(5)	Atm.	4	Three specimens. No reaction after considerable scratching. One specimen-reaction on unscratched titanium holding strip.
13(4)	Abt. 85(3)	26	Flow(5)	Atm.	2	No reaction.
14	Sat'd.(7)	26	Non-Flow	Atm.	1	No reaction after four hours of scratching.

(1) Specimen was vacuum annealed.
(2) Heating time was 70 minutes.
(3) Near saturated.
(4) A specimen with an electrolytically plus hydrochloric acid roughened surface.
(5) At a low flow rate that was not measured.
(6) Pressure raised in steps of about 2" of Hg and specimen scratched at each pressure.
(7) To assure saturation, liquid H_2O and then Cl_2 were added to evacuated reactor tube. Possible supersaturation.

When a fresh titanium surface is exposed to chlorine gas a very rapid reaction can result. Reactions initiated in non-flowing, bottled chlorine by scratching had the following general characteristics:

(a) A rainbow coloration would start at the point of initiation and then spread. Sometimes the color spread over the entire specimen surface. The time between the beginning color formation and the scratching varied from less than a minute to nearly an hour.

(b) A brown, liquid material would start to form in the scratch after color formation began and would continue to build up.

(c) A wet appearing, brownish film would start to form at the scratch and then spread gradually and tend to obscure the color formation.

(d) Sometimes surface pitting, generally near the scratch mark, occurred after the color spread and formation of brown material in the scratch mark was well advanced.

(e) After the color spread was well advanced and a considerable amount of brown material had formed in the scratch, the specimen would sometimes ignite. The product of the ignition reaction was titanium tetrachloride. Due to the small amount of chlorine available, the specimen was not destroyed. Figure 6 shows a sequence of such reactions up to the time of ignition. When sufficient water was present this reaction sequence did not occur.

The colored phase did not always start at the scratch. Sometimes it was at an edge or at the point of contact of the specimen and specimen holder. Under flow conditions the reaction tended to stop after initiation and there was a tendency for a white solid to form at reaction sites when there was an appreciable amount of water in the chlorine.

There was a difference in the makeup of the colored surface material when bottled chlorine was used and when dried, crude Hooker cell chlorine was used. Bottled chlorine produced a colored surface material that generally could be wiped off. Dried, crude Hooker cell chlorine, produced a colored material that was either more tenacious or could not be wiped off at all.

While investigating possible ways of accelerating the reaction between titanium and wet chlorine some observations were made. Specimens that were deeply pitted electrolytically and then further roughened by exposure to hydrochloric acid, reacted quite readily to chlorine that contained 0.11 percent water at room temperature in non-flow tests. No surface disturbance was required. When the hydrogen was removed from such a roughened surface by vacuum annealing at 1000 C (1832 F) it became much more resistant to chlorine. At room temperature with about 0.11 percent water in the chlorine no reaction occurred v the surface of the specimen was scratched. Al 155 C (311 F) was required before any reac was observed. In dry chlorine the reaction star readily with scratching. It appears that the rem of hydrogen increased resistance to chlorine att

Flow Scratch Tests

Flow scratch test reactions were not as dram as those in non-flow bottled chlorine. Often small spots of reaction occurred. Some typ reaction results are shown on specimens in Figu which also shows a specimen of unalloyed titan that withstood exposure to dry, static bot chlorine for 17 months with no evidence of react

In Table 3 are shown some data for flo bottled chlorine. In flowing, high purity chlo of about 0.85 percent water content one reac occurred in six tests. This reaction starte an unscratched titanium holder not on a specimen. Two specimens that did not react electrolytically roughened surfaces that reacted readily without scratching in non-flow chlorine of 0.11 percent water content. Th results show that because a reaction is l likely to occur in flowing chlorine, less wa is required for passivation.

Miscellaneous Tests

When 0.030-in diameter unalloyed titanium w was twisted until broken in the presence chlorine, either dry or saturated with wate

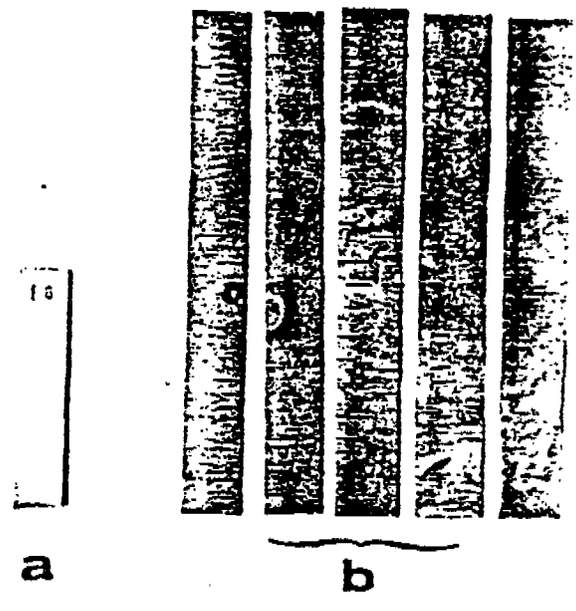


Figure 7 – A. Specimen of unalloyed titanium that had been e posed to dry, static chlorine at room temperature for 17 months without reacting. B. Specimens of unalloyed titanium that had been scratched in flowi dried, crude Hooker cell chlorine and showed vari degrees of attack from spot color formation to hea attack.

occurred, generally at the break point. mes a spot of white material would form g proceeded. There appeared to be no location for the appearance of these spots.

a jet of dry chlorine at room temperature at 0 psig was directed onto an unalloyed surface, no reaction occurred unless rifice tip touched the titanium surface. When chlorine was water-saturated no reaction red even when the surface was rubbed with of the glass orifice.

RESULTS OF SCRATCH TESTS IN HOOKER CHLORINE

Results of a large number of scratch tests r flowing, dried, crude Hooker cell chlorine shown in Figures 8, 9, 10 and 11. Chlorine rate had some effect in reducing the water quirements for inhibition of the reaction. This is most pronounced at room temperature and 175 C (346 F). There was less effect at 75 C 125 C (157-257 F). At higher temperatures water was very definitely required for tion of titanium in chlorine. In general the ing tests showed considerably less water required for inhibition than was necessary non-flow tests in purer chlorine.

Results of static and the flowing chlorine tests mparable. Static tests indicated between 0.71 percent water was required at temperature, while at low flow rates the ated content was about 0.4 percent. Static tests at 195 C (383 F) indicated that between 0.93 and 1.5 percent water was required. Tests at low flow rates and 175 C (347 F) indicated that about 1.1 percent water was required.

The small amount of oxygen in the Hooker Cell chlorine probably had an inhibiting effect beyond mere dilution but not in the same order as the effect of water.

Because the standard free energy of formation of TiO_2 is -203.8 Kcal and that of $TiCl_4$ (liq.) is -161.2 Kcal at 25 C it is likely that any reaction involving oxygen is directly with titanium, viz. $Ti + O_2 \rightarrow TiO_2$. The O_2 and Cl_2 are merely a mixture. With water and chlorine, however, there is probably some degree of chemical combination, such as the formation of hypochlorous acid, $H_2O + Cl_2 \rightarrow HCl \rightarrow HOCl$. It may be assumed that the brown liquid observed in some of the scratching tests was chlorine trioxide, ClO_3, which is a brown viscous liquid. This would require some degree of combination of water with chlorine. However, it is more likely that the brown material was wet titanium dichloride.

Among the scratching devices, Ti-6Al-4V alloy was the most satisfactory material. Stainless steel reacted to form a wet, green coating, probably of ferrous chloride. The diamond device chipped so that the cutting edge did not remain sharp. Glass rods broke. The Ti-6Al-4V alloy rod could be sharpened readily to produce a good scratch.

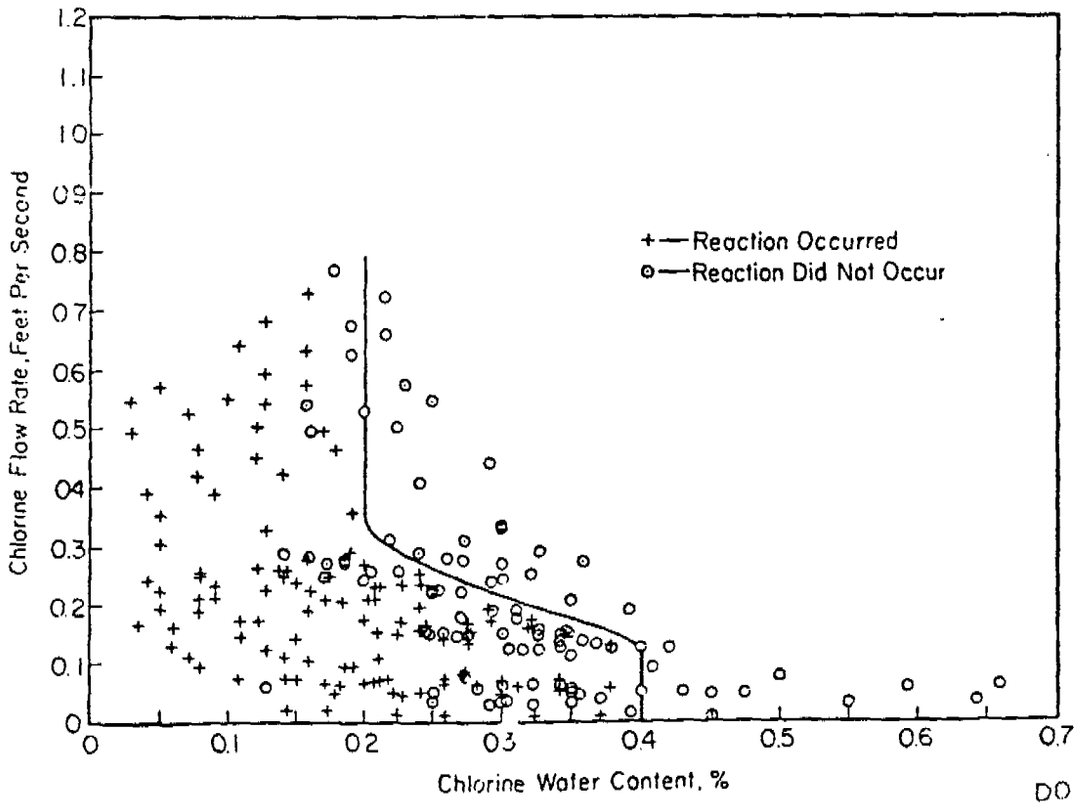


Figure 8 - Reactions occurring at room temperature in dried, crude Hooker cell chlorine.

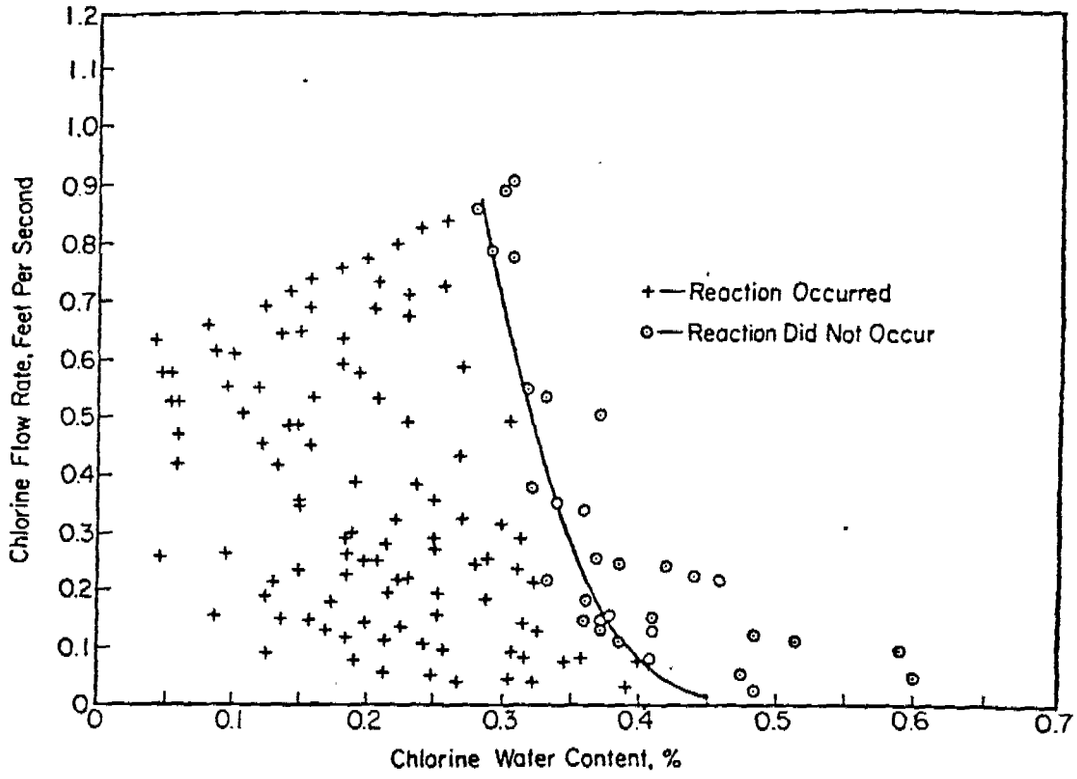
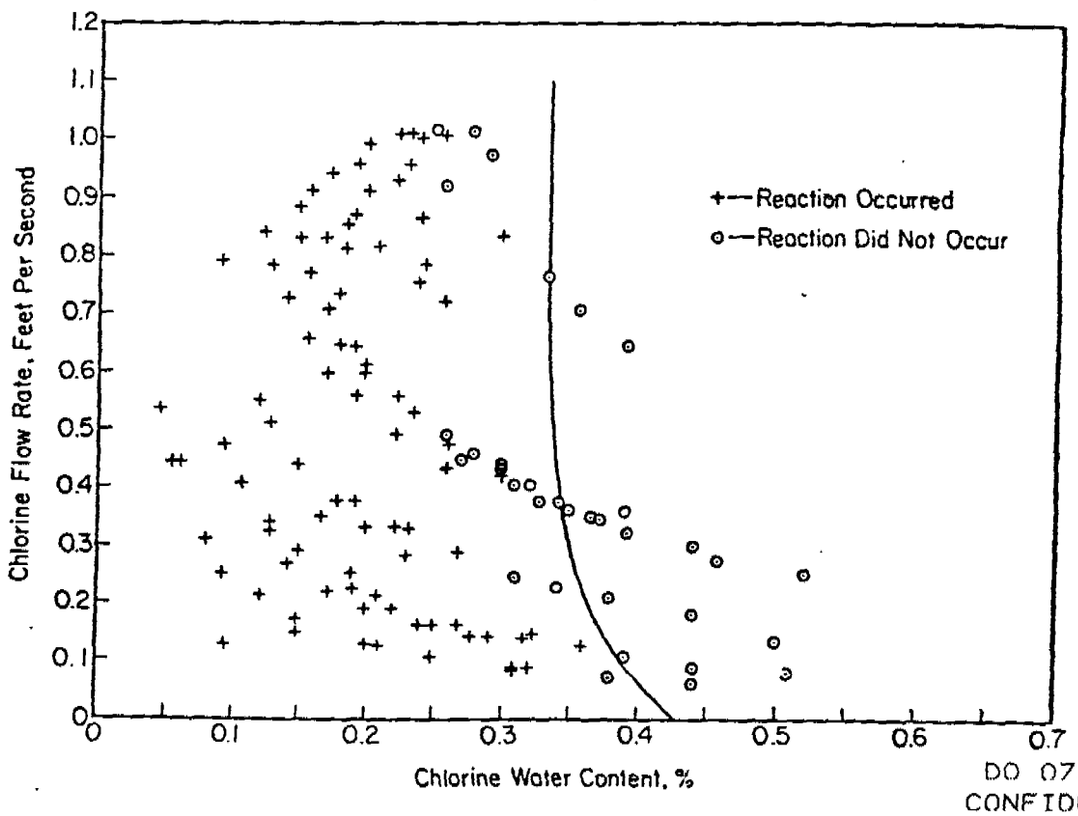


Figure 9 - Reactions occurring at 75 C in dried, crude Hooker cell chlorine.



DO 073043
CONFIDENTIAL

Figure 10 - Reactions occurring at 125 C in dried, crude Hooker cell chlorine.

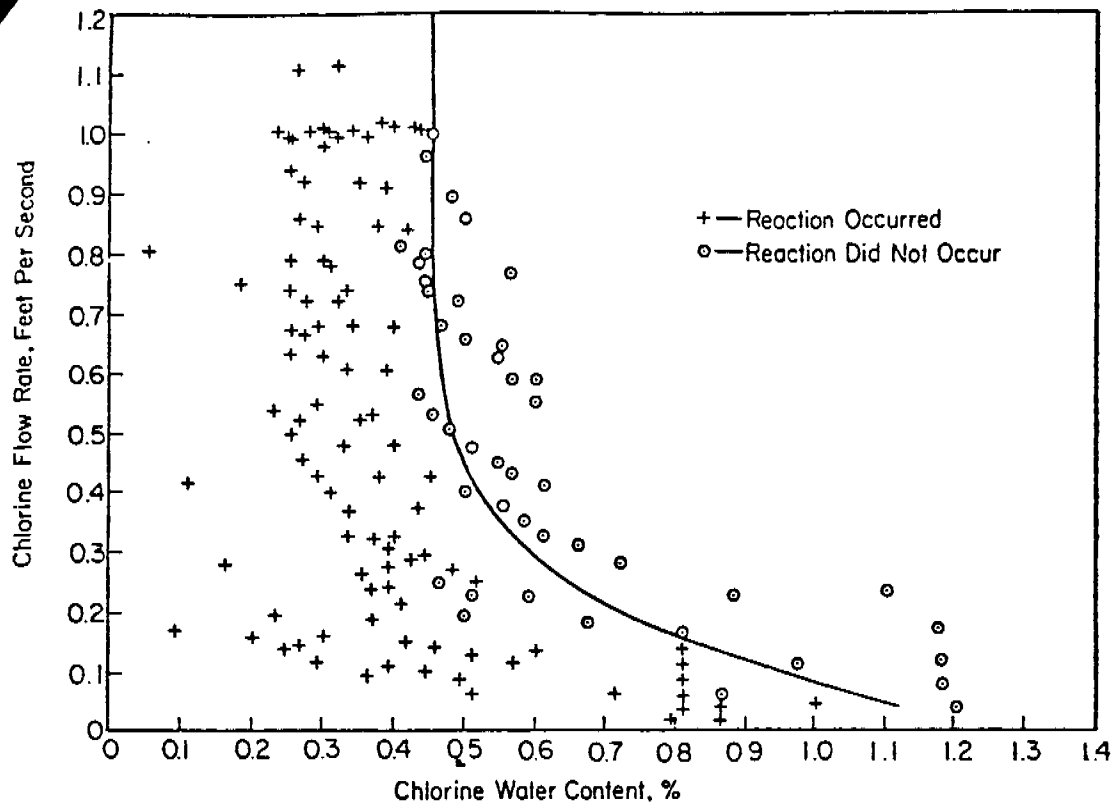


Figure 11 - Reactions occurring at 175 C in dried, crude Hooker cell chlorine.

To check the influence of surface preparation ... tests were made on specimens with no ... preparation, specimens that were heavily ...erprinted, some that were scrubbed with an ...sive cleaner and some that were scrubbed ... then pickled in 10 percent HNO_3-2 percent HF ...tion. The cleaner surfaces appeared to be ...ewhat more reactive, but the difference was ...ppreciable.

...hat appeared to be an important variable was ...ratch depth. A definite cutting action often ...ulted in reactions occurring under conditions ... none could be obtained with a dull scratching ...ace.

CONCLUSIONS

...lthough titanium is very sensitive to chlorine ..., a small amount of water will inhibit attack. ... amount of water required is a variable ...pending upon temperature, gas movement and ...ssure. Pure (99.5 percent) chlorine under ...atic conditions appears to require about 0.93 ...rcent water at room temperature. Somewhat ...s water is required if the chlorine is flowing. At higher temperatures to about 200 C (392 F) about 1.5 percent water is sufficient.

Flowing dried, crude Hooker cell chlorine did not require as much water for inhibition. At room temperature about 0.4 percent water was sufficient. At about 175 C (347 F), the amount of water required for passivation was about 1.1 percent or less, depending on the flow rate.

The amount of water required for protection of titanium is considerably higher than has been considered sufficient heretofore. Saturation may not be sufficient if the saturation value is below the required amount for a given set of conditions unless a film of water is present on the titanium surface.

Precise values for the degree of inhibition provided by a given amount of water are indeterminate because a reaction once started tends to be catastrophic. There is no easily measurable rate of corrosion. The water either does or does not prevent a reaction. It does not necessarily limit the rate of attack once a reaction has started unless a film of liquid water is present.

REFERENCES

...Titanium Summary. International Nickel Company.
...H. Uhlig. Corrosion and Corrosion Control. John Wiley ... Sons, New York, New York, 1963.
... Tech. Assoc. Pulp and Paper Ind., Vol. 44, 1B3A-8A ...01) February.
4. Private communication from another laboratory.
5. ASTM Standards, 1952. Part 2, Non-Ferrous Metals. American Society for Testing Materials, Philadelphia, Pa., p. 749.