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INHIBITION OF HASTELLOY B CORROSION

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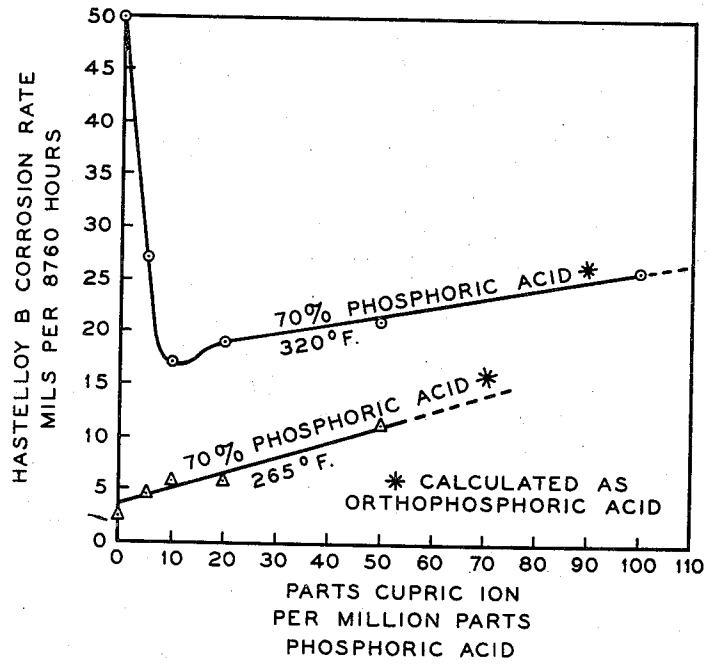


FIG. 1

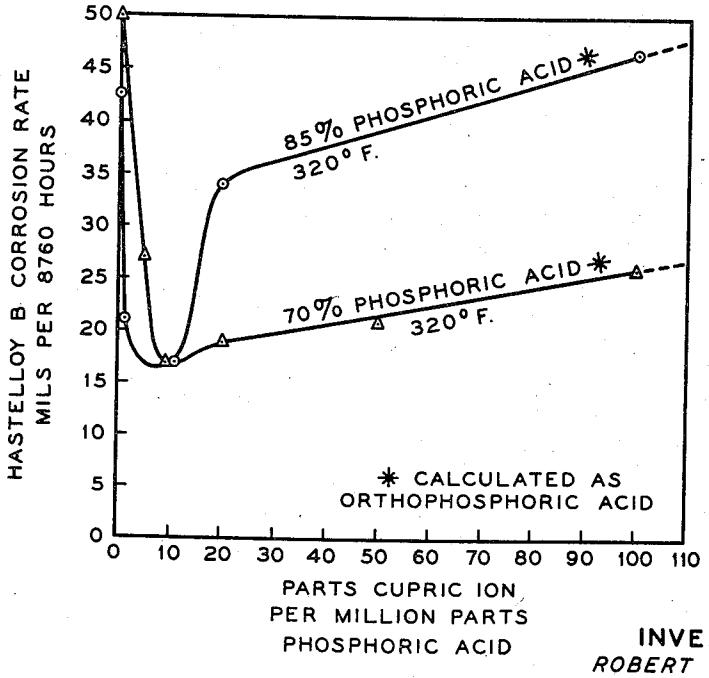


FIG. 2

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INHIBITION OF HASTELLOY B CORROSION

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4 Claims. (Cl. 260—683.15)

This invention relates to a method for inhibiting the corrosive attack of concentrated liquid phosphoric acid on certain nickel-molybdenum alloys, and more particularly to a method for retarding the rate at which certain nickel-molybdenum alloys containing less than about 10% of other metals, primarily as impurities, are corrosively attacked by liquid phosphoric acid.

This invention is especially concerned with retarding or inhibiting the rate at which liquid phosphoric acid corrosively attacks one of these alloys that is known commercially as "Hastelloy B," and which has the following composition:

Constituent:	Weight percentage
Molybdenum	26–30%.
Iron	4–7.
Silicon	1.0 max.
Carbon	0.12 max.
Chromium	1.0 max.
Manganese	1.0 max.
Nickel	Balance.

Liquid phosphoric acid is recognized as an efficient catalyst for certain organic chemical reactions, including certain alkylation and isomerization reactions and the polymerization of normal gaseous olefins. For these reactions it is frequently necessary to employ reaction vessels, auxiliary equipment and connecting lines that present metal surfaces to the phosphoric acid catalyst and thus become subject to progressive corrosive attack by the acid. In order to minimize such corrosive attack, the equipment is desirably constructed of highly acid-resistant alloys, especially those nickel-molybdenum alloys containing less than about 10% of other metals. Among such alloys, Hastelloy B heretofore has been employed with considerable success, and the invention will be particularly described hereinafter as it relates to this exemplary nickel-molybdenum alloy.

Hastelloy B, developed to resist certain severe conditions of chemical corrosion, is so highly resistant to corrosive attack by phosphoric acid that it is equalled in this respect by few other metals. Notwithstanding this fact, liquid phosphoric acid, especially at elevated temperatures, high acid ester content, and relatively low acid concentrations, is so highly corrosive, to Hastelloy B that it can seriously shorten the life of equipment fabricated therefrom. This life should be at least five years (and preferably more) to be considered satisfactory from an efficient process operation standpoint. A five-year life reasonably can be predicted for the Hastelloy B components of process equipment of standard construction if these components do not corrode at a rate greater than about 50 mils per year of continuous operation, i. e., about one-twentieth inch per 8760 hours. At this corrosion rate five years would be required for the corrosion to proceed one-quarter inch.

The foregoing maximum tolerable corrosion rate of Hastelloy B in the past has been a serious limitation on process flexibility, especially in polymerization processes employing liquid phosphoric acid as a polymerization catalyst. Process flexibility in these processes requires that acid concentrations be lowered where necessary to prevent the formation of certain heavier polymer products and that process temperatures be raised to increase polymerization efficiency. However, the making of either of these changes results in a marked increase in the corrosion rate of the Hastelloy B that is exposed to the phosphoric acid, and in a corresponding shortening of the life of the process equipment embodying that alloy. To make both changes even more quickly shortens the process equipment life, because the combined effect of the changes on the corrosion rate of the Hastelloy B is cumulative.

Bearing in mind the foregoing conflict between a tolerable Hastelloy B corrosion rate and a required flexibility of acid concentration and process temperature, it is an object of this invention to provide a method whereby the corrosion rate of Hastelloy B in contact with liquid phosphoric acid can be maintained within acceptable limits even when employed at relatively high process temperatures and low acid concentrations.

I have found by a series of tests, the data from which are set forth and discussed hereinafter that, within certain ranges, the addition of small quantities of cupric ion to liquid phosphoric acid at relatively elevated temperatures and acid concentrations will cause the corrosion rate of Hastelloy B in contact with the phosphoric acid to decrease, pass through a minimal value and then rise. This result takes place at acid concentrations of about 70% and above (expressed as H_3PO_4), cupric ion concentrations in the range of from about 2–25 p. p. m., and temperatures substantially above 265° F., preferably at least 290° F. By maintaining the cupric ion concentrations at certain acid temperatures and concentrations in the corrosion-inhibiting range so found, previously limiting acid temperatures may be raised and acid concentrations lowered to the extent that the increase in the corrosion rate of the Hastelloy B attributable to those changes equals the reduction in corrosion rate of the Hastelloy B attributable to the presence of the cupric ion.

It is quite unexpected thus to find that certain concentrations of cupric ion in the acid will inhibit the corrosion of Hastelloy B, in view of prior art statements that strong oxidizing agents such as copper will always accelerate the corrosive attack of liquid phosphoric acid on Hastelloy B. For example, in "Chemical Engineering" for July 1952, at page 316 of an article in the Corrosion Forum, it is said, "The major resistance displayed by Alloy B (Hastelloy B) is to reducing conditions. Strongly oxidizing agents are to be avoided. The presence of cupric, ferric, or other oxidizing ions tend to accelerate attack of the alloy."

In the tests reported in Table I the cupric ion was added as basic cupric carbonate, $CuCO_3.Cu(OH)_2$, which reacted with the phosphoric acid to liberate CO_2, thus removing any interfering anions from the solution. Since the amount of copper compound added is very small, other copper compounds may be used instead of the cupric carbonate without producing any significant change in the catalytic activity of the acid-copper solution. For example, copper phosphate ($Cu_3(PO_4)_2.3H_2O$) or other copper salts may be used.

Data in the following table were obtained in the above-mentioned tests, wherein samples of Hastelloy B were exposed to phosphoric acid solutions at the concentrations and temperatures noted in the table.

Table I

Temperature in ° F.	265	320	320	450
Percent Phosphoric Acid [1]	70	70	85	100
Parts Per Million of Cupric Ion In Phosphoric Acid		Corrosion Rate In Mils Per Year of Hastelloy B		
0	2.6	50	[2] 35–50	14.4
2			21	
5	4.6	27	15	9.8
10	5.9	17	[2] 15–19	7.3
20	5.9	19	34	3.8
50	11.4	21		4.8
100		26	[2] 45–48	
500		50		
1,000			200	

[1] Calculated as orthophosphoric acid.
[2] Range of values obtained in two or more tests.

The data from the above table may be seen in more graphic form, further objects and advantages of the invention will be more apparent, and the following discussion of the invention will be more clearly understood, by reference to the appended drawings, in which:

Fig. 1 is a graphical representation comparing the effects of two different temperatures on Hastelloy B corrosion rates at various cupric ion concentrations and constant acid concentrations; and

Fig. 2 is a graphical representation comparing the effects of two different acid concentrations on Hastelloy B corrosion rates at various cupric ion concentrations and constant temperatures.

Referring now to Fig. 1, there shown graphically is the effect on Hastelloy B corrosion rate of the addition to 70% phosphoric acid (calculated as orthophosphoric acid) of various quantities of cupric ion at two different temperatures, viz., 265° F. and 320° F. It may be seen from a comparison of the lower and upper curves that, regardless of the cupric ion concentration, but particularly in the absence of cupric ion, an increase in temperature increases the Hastelloy B corrosion rate. Therefore, when a process was heretofore operated at or near tolerable Hastelloy B corrosion rates, a further temperature increase to increase process efficiency was precluded, because such increase would cause the tolerable Hastelloy B corrosion rates to be exceeded.

It may also be seen from Fig. 1 that at the lower temperature of 265° F., the addition to 70% acid of progressively greater quantities of cupric ion over a range of 0 to 50 p. p. m. of cupric ion was accompanied by a virtually linear increase in the corrosion rate of Hastelloy B rather than by a decrease. Thus, at this temperature (as well as at lower temperatures, where the results are essentially the same) the use of copper ion is to be avoided. However, an examination of the upper curve in Fig. 1 discloses that totally unexpected results are obtained on adding progressively larger quantities of cupric ion to the acid at the higher temperature of 320° F. First, the curve shows that at this temperature and zero cupric ion concentration, the above-discussed tolerable Hastelloy B corrosion rate of 50 mils per year is already reached and would be exceeded by a further temperature increase (or a decrease in acid concentration). However, a sharp drop in corrosion rate is obtained with the addition of small quantities of cupric ion. Addition of 5 p. p. m. of cupric ion results in approximately halving the corrosion rate, while the addition of 10 p. p. m. of cupric ion decreases the corrosion rate to but 17 mils per year, a decrease of approximately 60% over the corrosion rate prevailing in the absence of cupric ion. At this point the further addition of cupric ion causes the curve to pass through a minimal corrosion rate value and take an unexpected upward turn. Thereafter, the addition of cupric ion causes a progressive corrosion rate increase.

Referring now to Fig. 2, there shown graphically is the effect on Hastelloy B corrosion rate of the addition of

various quantities of cupric ion to 70% phosphoric acid and 85% phosphoric acid, in each case calculated as orthophosphoric acid, and in each case at a temperature of 320° F. It may be seen from a comparison of the upper and lower curves that below a cupric ion concentration of about 10 p. p. m., a decrease in acid concentration from 85% to 70% increased the Hastelloy B corrosion rate. This is in accord with the general theory, but only insofar as cupric ion concentrations of less than about 10 p. p. m., are concerned. At concentrations above this amount, the higher acid concentration results in a higher corrosion rate, an effect which does not accord with the general theory.

From the foregoing it may be seen that a marked decrease in the corrosion rate of Hastelloy B surfaces exposed to phosphoric acid can be obtained, particularly at temperatures above about 290° F. and at acid concentrations of about 70% or more, by maintaining from about 2 to 25 p. p. m., of cupric ion in the solution, with especially good results being maintained in many cases when the amount of cupric ion maintained in the solution falls in the range from about 5 to 15 p. p. m. While the benefits of such copper addition are less marked in the case of phosphoric acids having a concentration of 100% or more since such acids have a relatively low rate of attack on Hastelloy B even in the absence of copper, nevertheless even here the maintenance in the acid of cupric ions within the 2–25 p. p. m. range is quite effective in reducing the corrosion rate, as evidenced by the data in Table I above.

While in the above discussion only commonly used temperatures and acid concentration ranges have been discussed, those skilled in the art will be able to perceive numerous other temperature and acid concentration ranges with which the methods of this invention may be used without departing from the spirit thereof. All such ranges, and other modifications and variations of the methods of this invention that will be apparent to those skilled in the art are intended to be embraced by the following claims.

I claim:

1. In an organic conversion process wherein a Hastelloy B alloy is in contact with liquid phosphoric acid at such acid temperature and concentration combinations, of at least 290° F. and 70% (calculated as ortho-phosphoric acid), respectively, that addition of some quantities of cupric ion to said acid will reduce the rate of corrosive attack of acid on said alloy, the method of enabling said process to be operated at a lower acid concentration without an increase in the rate of said corrosive attack, which comprises maintaining in said acid an amount of from about 2 to 25 parts of cupric ion per million parts of said acid.

2. In an organic conversion process catalyzed by phosphoric acid at concentrations of at least 70% calculated as orthophosphoric acid, said process being conducted at temperatures of at least about 290° F. in a conversion zone having metal surfaces in contact with said phosphoric acid, said metal surfaces comprising a molydenum-nickel alloy containing 26–30% molybdenum, 4–7% iron, 0.02–0.12% carbon, not more than 1.0% silicon, not more than 1.0% chromium, not more than 1.0% manganese, and a balance of nickel, the method of inhibiting corrosive attack of said metal surfaces by said acid which comprises maintaining in said acid between 2 and 25 parts of cupric ion per million parts of said acid.

3. The method of inhibiting the corrosive effects of liquid phosphoric acid having a concentration of at least 70% calculated as orthophosphoric acid at temperatures above about 290° F. on an alloy containing 26–30% molybdenum, 4–7% iron, 0.02–0.12% carbon, not more than 1.0% silicon, not more than 1.0% chromium, not more than 1.0% manganese, and a balance of nickel, which comprises maintaining in said acid a cupric ion

concentration of between 2 and 25 parts of cupric ion per million parts of said acid.

4. The method of inhibiting the corrosive effects of liquid phosphoric acid at concentrations of at least 70% calculated as orthophosphoric acid, and at temperatures above about 290° F. on an alloy containing 26–30% molybdenum, 4–7% iron, 0.02–0.12% carbon, not more than 1.0% silicon, not more than 1.0% chromium, not more than 1.0% manganese, and a balance of nickel,

which comprises providing in said acid an initial cupric ion concentration between about 2 and 25 parts of cupric ion per million parts of said acid.

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