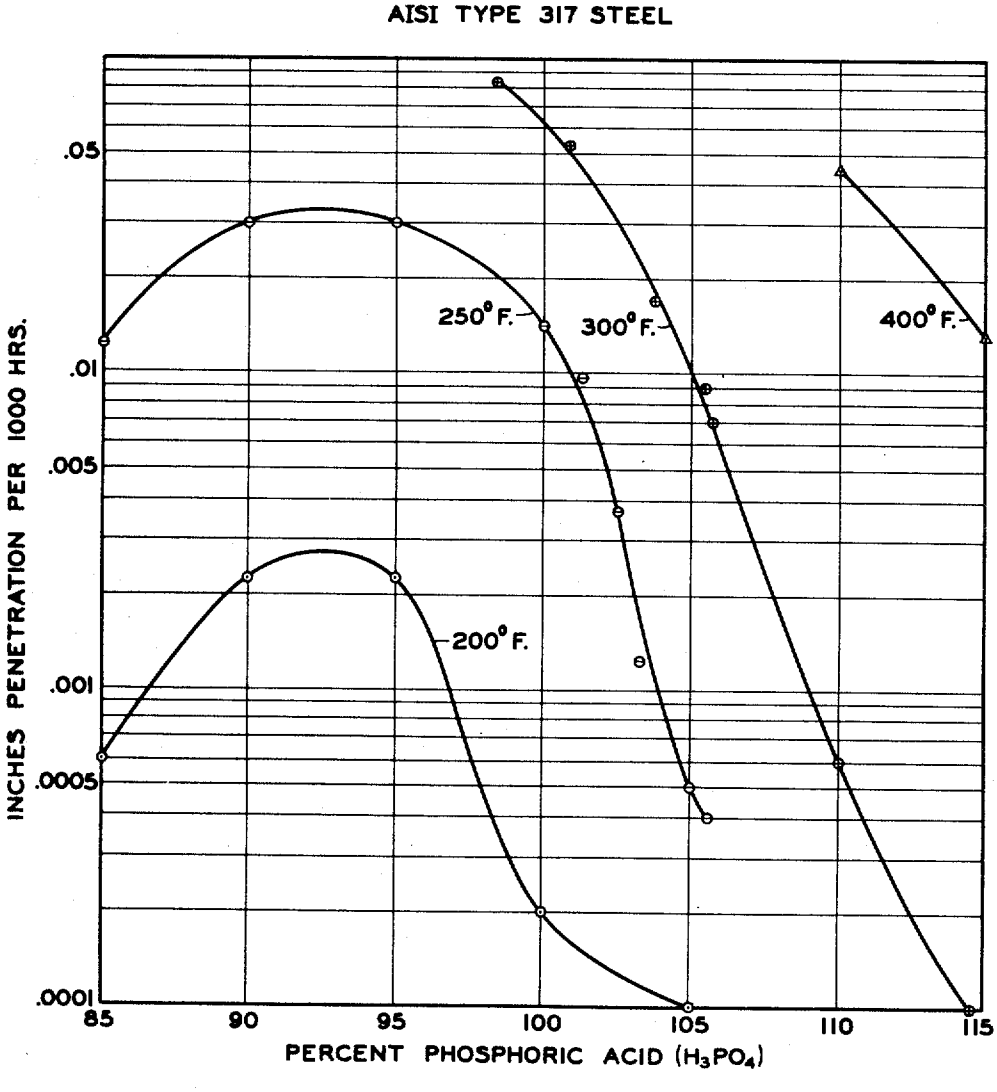
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INHIBITION OF PHOSPHORIC ACID CORROSION

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INVENTORS
Jacob D. Kemp
Henry P. Zeh
BY:
ATTORNEYS

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INHIBITION OF PHOSPHORIC ACID CORROSION

Jacob D. Kemp, Richmond, and Henry P. Zeh, Berkeley, Calif., assignors, by direct and mesne assignments, to California Research Corporation, San Francisco, Calif., a corporation of Delaware

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1 Claim. (Cl. 260—683.15)

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This invention relates to a method for inhibiting the corrosive attack of concentrated phosphoric acid upon high chrome-nickel austenitic steels containing molybdenum, and more particularly, to a method of inhibiting such attack during hydrocarbon reactions catalyzed by phosphoric acid at concentrations above about 100% calculated as orthophosphoric acid and conducted at temperatures above about 200° F. in reaction vessels constructed from or lined with such steels.

Liquid phosphoric acid is known to be an efficient catalyst for certain organic reactions such as the alkylation of aromatics with olefins, the isomerization of olefins, and especially for the polymerization of normally gaseous olefins. The corrosive attack of phosphoric acid upon the various materials available for construction of reaction vessels suitable for conducting such reactions is so rapid that this catalyst has not heretofore been employed in commercial alkylation, isomerization, or polymerization units.

It is an object of this invention to provide a method for inhibiting the attack of concentrated phosphoric acid on high chrome-nickel austenitic steels containing molybdenum.

It is a further object of this invention to provide a combination of a material of construction, an acid concentration of phosphoric acid, and a corrosion inhibitor which makes possible the commercial polymerization of normally gaseous olefins catalyzed by liquid phosphoric acid in which the process hazards and unfavorable economic effects of corrosion are substantially eliminated.

High chrome-nickel austenitic steels containing molybdenum are readily available as materials for the construction of commercial scale reaction vessels. They are inherently acid resistant, and problems of fabricating of these steels are well understood. They have been successfully employed in the construction of a variety of commercial articles and vessels large and small and are eminently suitable for the construction of reaction vessels and connecting lines for

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processes employing concentrated phosphoric acid as a catalyst when the rate of their corrosion is reduced in the manner hereinafter described.

By the term "high chrome-nickel austenitic steels containing molybdenum" as used herein, it is intended to include austenitic steels containing at least 16% and up to about 30% of chromium, containing at least 7% and up to about 20% of nickel, containing at least ½ of 1% and up to about 8% and preferably between 1% and 5% of molybdenum and containing not in excess of $\frac{1}{10}$ of 1% carbon. AISI types 316 and 317 steel are illustrative of commercially available high chrome-nickel austenitic alloys containing molybdenum. Type 316 contains 16 to 18% chromium, 10 to 14% nickel, 2 to 3% molybdenum, a maximum of $\frac{1}{10}$ of 1% carbon, and the remainder iron. Type 317 metal contains 18 to 20% chromium, 10 to 14% nickel, 3 to 4% molybdenum, a maximum of $\frac{1}{10}$ of 1% carbon, and the remainder iron. These two particular alloys and other alloys falling within the broader range of composition set forth above may be made highly resistant to the corrosive attack of concentrated phosphoric acid by the addition to the acid of minor amounts of dissolved copper.

It has been found that the attack by phosphoric acid on high chrome-nickel steels containing molybdenum is markedly decreased at acid concentrations above about 100% calculated as orthophosphoric acid. A number of test runs were made in which type 317 steel was exposed to the attack of concentrated phosphoric acid at concentrations in the range 85–115% and the temperatures within the range 200–400° F. The concentration of the phosphoric acid is determined by titrating a weighed sample of acid with a base of known concentration. From the titration the weight of orthophosphoric acid equivalent to the base consumed is calculated and the concentration of the sample is then determined by dividing the calculated weight by the measured weight of the sample and expressing the result as per cent orthophosphoric acid.

The results of these tests are summarized in the attached figure, which is a graphical representation of the variation of corrosion rate with acid concentration at a variety of temperatures. From the figure it is seen that as the acid concentration rises above about 95% and especially when it is above 100%, the rate of corrosive attack decreased very rapidly as the acid concentration is increased. The figure clearly shows that a considerable degree of control may be exercised over the rate at which high chrome-nickel austenitic alloys containing molybdenum are attacked by phosphoric acid by making a suitable selection of temperature and acid concentration. A maximum tolerable corrosion rate of 0.01 inch per thousand hours may be set, based on considerations of economy and safety, and if corrosion is maintained at or below this rate, a process life of approximately 5 years can be obtained in a vessel or pipe having a high chrome-nickel lining ½ inch in thickness. If the acid concentration employed in the process is sufficiently high, as indicated by the attached figure, tolerably low corrosion may be insured at temperatures up to about 325° F. Where the acid is employed as a catalyst for the polymerization of normally gaseous olefins, this method of controlling corrosion requires the sacrifice of a considerable degree of process flexibility, since the high acid concentrations which are required to control corrosion are accompanied by a tendency toward the production of a heavier polymer product than could be obtained with acids at lower concentration.

In addition to the effect of acid concentration on the corrosion rate indicated above, it has been found that the addition of small amounts of copper to the acid causes a marked decrease in the rate of corrosion of high chrome-nickel austenitic steels containing molybdenum. When copper is dissolved in phosphoric acid at concentrations above 100%, the combined effects of the high acid concentration and the presence of copper on the corrosion rate extends the range of acid concentration which may be employed at any given temperature while maintaining the corrosion rate well below 0.01 inch per thousand hours. The use of copper with very concentrated phosphoric acid, for example 110% acid, makes it possible to conduct the catalytic polymerization of olefins at temperatures up to about 375° F. without exceeding 0.01 inch of corrosive penetration per 1000 hours. This combined effect increases the flexibility of a process such as polymerization of normally gaseous olefins and greatly extends the duration of the apparatus life.

It has further been found that if the high chrome-nickel austenitic steels containing molybdenum have either a low carbon content below 0.03% or contain columbium in an amount equal to about 10 times the carbon content, but not greater than 1%, or contain titanium in an amount equal to about 4 times the carbon content but not greater than 1%, then, not only is ordinary corrosion occasioned by the attack of the acid reduced by the addition of copper, but also intergranular corrosion does not occur. This is a significant aspect of the employment of copper to inhibit corrosion of high chrome-nickel austenitic alloys by phosphoric acid, since it is known that the immersion of stainless steels in a boiling solution of sulfuric acid and copper sulfate (Strauss solution) greatly accelerates the rate of intergranular corrosion. It is believed that intergranular corrosion, which results in intercrystalline cracking of the material, is produced by solutions tending to form a protective film over the crystal surfaces of the material while they attack the grain boundaries of the material. Intergranular corrosion is especially significant and serious where the material under consideration is used in the construction of vessels in which reactions are carried out at an elevated pressure.

A series of tests was conducted in which ordinary corrosion rates and the incidence of intergranular corrosion were determined in regular AISI type 316 and 317 steels containing about 0.07% carbon. Half of the specimens were heat treated at 1100° F. for 24 hours to make them highly susceptible to intergranular corrosion and the other half were given a stress-relief treatment at 1300° F. for 7 hours. All the specimens were exposed for a total of 840 hours in 104% phosphoric acid at 300° F. The results of these tests are summarized in the following Table I.

TABLE I

Corrosion resistance of regular type 316 and 317 steels exposed in 104% phosphoric acid at 300° F. for 840 hours

Material	Heat Treatment	Grams of Dissolved Copper/l.	Intergranular Corrosion	Corrosion Rate in Inches Pen. Per 1,000 Hours
Type 317	1,150° F. for 24 hrs	0.0	None	0.016
Do	do	0.1	do	.010
Do	1,300° F. for 7 hrs	0.1	do	.009
Do	1,150° F. for 24 hrs	0.3	do	.007
Do	1,300° F. for 7 hrs	0.3	do	.007
Do	1,150° F. for 24 hrs	0.9	do	.002
Do	1,300° F. for 7 hrs	0.9	do	.0015
Do	1,150° F. for 24 hrs	2.6	do	.003
Type 316	do	0.1	Yes	.006
Do	1,300° F. for 7 hrs	0.1	Slight	.006
Do	1,150° F. for 24 hrs	0.3	Yes	.005
Do	1,300° F. for 7 hrs	0.3	Yes	.005
Do	1,150° F. for 24 hrs	0.9	Yes	.006
Do	1,300° F. for 7 hrs	0.9	None	.005
Do	1,150° F. for 24 hrs	2.6	Yes	.004

Data summarized in the above table show that the reduction in corrosion by the addition of one gram of copper per liter of acid was very effective for regular type 317 steel; the rate was 0.002 inch per thousand hours. The lowest rate observed for the regular type 316 steel was 0.005 inch per thousand hours; in this case the copper addition was not as effective as in the case of the type 317. The type 317 steels appeared to be completely immune to intergranular corrosion, whereas the type 316 specimens were not. It is not believed that the additional molybdenum in the type 317 steel was responsible for its immunity to intergranular corrosion, since molybdenum usually has little effect in this direction. Rather, it is believed that longer exposure of the type 317 steel would have produced incipient intergranular corrosion. The addition of copper clearly reduces the ordinary rate of corrosion of regular type 316 and 317 steels, but if their use in pressure apparatus were contemplated, intergranular corrosion might present a hazard.

In a second series of tests, 14 samples of type 316 and type 317 steels having either a low carbon content below 0.03%, or containing up to 1% of columbium, the columbium content being approximately 10 times the carbon content, were heat treated at 1100° F. for 24 hours to induce susceptibility to intergranular corrosion, and were then exposed to 104% phosphoric acid containing approximately 1 gram per liter of dis-

solved copper at 300° F. for 840 hours. The results of this series of tests are summarized in the following Table II:

TABLE II

Effect of copper on the corrosion resistance of low carbon (0.03% max.) and columbium (1% max.) stabilized type 316 and type 317 steels exposed in 104% phosphoric acid at 300° F. for 840 hours

[The acid contained 0.9 gram per liter of dissolved copper in all of the tests. All specimens were heated for 24 hours at 1150° F. to obtain maximum sensitivity to intergranular corrosion.]

Material	Intergranular Corrosion	Corrosion Rate in Inches Pen. Per 1,000 Hours
Type 316 low C	None	0.002
Do	do	.002
Do	do	.001
Type 317 low C	do	.001
Do	do	.002
Do	do	.003
Do	do	.001
Type 316 Cb	do	.0015
Do	do	.002
Do	Yes [1]	.004
Do	None	.001
Do	do	.003
Type 317 Cb	do	.003
Type 317, 0.04 C	Yes	.0015

[1] Microscopic examination indicated that this alloy did not contain sufficient columbium for stabilization.

The results summarized in the above table show that all of the alloys containing 0.03% carbon or less and also those containing sufficient columbium for stabilization were resistant to intergranular corrosion. Ordinary corrosion rates also were satisfactory, falling well below the arbitrary practical maximum of 0.01 inch per thousand hours.

A third series of tests was conducted to determine the effect of copper on corrosion by 104% phosphoric acid at 350° F. Both regular and low carbon type 317 specimens were subjected to the attack of the acid after heat treatment to induce susceptibility to intergranular corrosion. Results are summarized in the following Table III:

TABLE III

Effect of copper on the corrosion resistance of regular and low carbon type 317 steels in 104% phosphoric acid at 350° F. for 20 hours

Material	Grams of Dissolved Copper/l.	Corrosion Rate in Inches Pen. Per 1,000 Hours
Type 317	0.0	0.18
Type 317 low C	0.0	.22
Type 317	0.1	.047
Type 317 low C	0.1	.053
Type 317	0.3	.031
Type 317 low C	0.3	.038
Type 317	0.9	.009
Type 317 low C	0.9	.012

From the foregoing data, it will be seen that the addition of copper reduced the corrosion rate from 0.2 inch to 0.012 inch per thousand hours when about 1 gram of copper per liter of acid was present. Corrosion rates of the low carbon alloy are slightly higher than those of the regular alloy, but the difference is not significant.

From the data obtained in similar experiments, it is concluded that the presence of dissolved copper in amounts in excess of about 0.05 gram per liter of acid have a significant effect in reducing the ordinary corrosive attack of phosphoric acid upon high chrome-nickel alloys containing molybdenum. This reduction in ordinary corrosion is accompanied by an absence of any tendency toward intergranular corrosion, where either the carbon content of the alloys is below 0.03% or where stabilizing amounts of columbium or titanium up to about 1% are included in the alloy.

The amount of copper which is added to the acid to inhibit corrosion in this manner is preferably in the range 0.05 gram to 2.5 grams of copper per liter of acid, the usual amount being approximately 1 gram per liter. Larger quantities of copper might be added, but relatively little effect is produced on the rate of corrosion by the addition of copper in amounts in excess of about 1 gram per liter. Further, there is an indication that the addition of larger amounts of copper may undesirably affect the quality of the polymer product produced when the acid containing the dissolved copper is employed to catalyze the polymerization of normally gaseous olefins.

The copper is added to the acid usually in the form of copper phosphate ($Cu_3(PO_4)_2 \cdot 3H_2O$), since the addition of this compound does not involve the introduction of negative ions other than the phosphate ion into the acid catalyst. Since the amount of the copper compound added is very small, other copper compounds than the phosphate may be added to the acid without producing any significant change in the catalytic activity of the acid-copper solution.

The employment of 0.05 to 2.5 grams per liter of dissolved copper in phosphoric acid at concentrations of 103.2%, 104.9%, 105.4%, 106.4%, and 110.3% calculated as orthophosphoric acid was found to inhibit corrosion of type 316 and type 317 steels during the polymerization of propylene and of propylene-butene mixtures at temperatures in the range 200° to 375° F. and at pressures in excess of 200 p. s. i. g. The employment of the copper inhibitor in the acid catalyst in these amounts was not found to have any detectable effect on conversion rates of the mono-olefins nor on the quality of the polymer produced.

The following example illustrates the effectiveness of copper to inhibit the corrosion of type 317 steel during the polymerization of propylene. A gas consisting essentially of propylene and propane and containing 44.2% by volume of propylene was intimately contacted with phosphoric acid in a continuous run of 33 hours duration. The gas introduced into the acid in liquid phase and the acid and hydrocarbon were vigorously stirred together. A mixture of acid and hydrocarbon was continuously withdrawn and settled. The hydrocarbon was removed as a product and the acid was returned to the reactor. The acid had an initial concentration of 103.2% and contained 2.1 grams of dissolved copper per liter of acid. The reaction was conducted at 300° F. and at a pressure of 360 p. s. i. g. The feed was introduced at a rate of 1.7 volumes of liquid propylene per volume of acid per hour and conversion was 85.2%. The product consisted predominantly of C_9–C_{15} polymers and had an end point of 510° F. with 99% overhead. The corrosion rate of type 317 metal during the run was 0.0018 inch per 1000 hours.

Copper was similarly effective in reducing corrosion of high chrome-nickel austenitic steels containing molybdenum during the polymerization of butenes and mixed propylene-butene feeds by contact with phosphoric acid at 100% and higher concentrations.

We claim:

In an organic conversion process catalyzed by phosphoric acid at concentrations in excess of 100% calculated as orthophosphoric acid conducted at temperatures of at least 200° F. and superatmospheric pressures in a reaction vessel presenting metal surfaces in contact with said phosphoric acid of an austenitic steel containing 16–30% chromium, 7–20% nickel, at least ½% molybdenum and not in excess of 0.03% carbon, the method of inhibiting corrosive attack of said steel by said acid without inducing intergranular corrosion which comprises maintaining in solution in said acid a minor amount of copper between about 0.05 and 2.5 grams per liter of acid.

JACOB D. KEMP.
HENRY P. ZEH.

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