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CORROSION INHIBITORS FOR AQUEOUS ACIDS

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This invention relates to synergistic combinations of acetylenic alcohols as corrosion inhibitors for aqueous solutions of non-oxidizing acids.

Propargyl alcohol is well known as a corrosion inhibitor. Its higher homologs also are active inhibitors. In view of this prior knowledge, it would be expected that mixtures of acetylenic alcohols such as propargyl alcohol and its homologs would exhibit additive inhibition in aqueous acids. However, it has now been discovered that mixtures of acetylenic alcohols, that is, propargyl alcohol and its homologs, are synergistically effective as corrosion inhibitors. This unexpected discovery permits the inhibition of aqeuous acid solutions by use of a smaller total amount of inhibitor than is possible when using only one of the acetylenic alcohols.

In many applications, such as metal cleaning and oil well acidizing, aqueous acids are in contact with metals at elevated temperatures. In these applications it has been found that many corrosion inhibitors that are effective at ordinary temperatures fail at the higher temperatures. Accordingly, it is common practice to evaluate inhibitors at elevated temperatures, it being known that those thus found to be effective will also be effective at

lower temperatures. Likewise, it is common practice to evaluate inhibitors in 15% aqueous hydrochloric acid, since it has been found that other non-oxidizing acids give similar results and the effect of concentration is well known; i.e., corrosion gradually increases as the acid concentration is increased, at least in the range of concentration up to 50%.

The preferred acetylenic alcohols are those corresponding to the formula

$$C_nH_{2n+1}—CHOH—C{\equiv}CH$$

wherein n is an integer from 0 to about 8.

Many alcohols having the above formula are known and methods for the preparation of such compounds are likewise known. A convenient and well-known procedure for their synthesis consists of condensing the appropriate aldehyde, $C_nH_{2n+1}—CHO$, with sodium acetylide. The preferred aldehydes are those having unbranched carbon chains, although the unexpected synergistic result is also obtained with branched chain alcohols.

To illustrate the practice of the invention and to demonstrate the synergistic corrosion inhibition effected by the compositions of the inventions, a series of standardized corrosion tests were run under controlled conditions.

Procedure.—The metal coupons were suspended in the acid solution containing the inhibitor for the specified time and at the specified temperature. The coupons were then removed, rinsed, dried and weighed to determine the weight of metal lost during the test. From this and the surface area of the coupon, the corrosion rate was calculated as lbs. per. sq. ft. per day. Results of same typical tests are shown in Table I.

TABLE I.—EFFECT OF VARIOUS ALKYNOLS AND MIXTURES THEREOF AS CORROSION INHIBITORS IN HYDROCHLORIC ACID

Acid media—150 ml. of 15% hydrochloric acid
Metal—AISI 1010 mild steel coupon (0.12" x 1.0" x 2.75")
Temperature—200° F.
Length of test—16 hours

Test	Concentration alkynol[a] (percent by volume)							Corrosion rate (lbs./ft.²/day)
	Propynol	Butynol	Pentynol	Hexynol	Heptynol	Nonynol	Decynol	
1	0.4							0.02
2	0.2							1.0
3		0.4						0.02
4		0.2						1.0
5			0.4					0.005
6			0.2					0.015
7				0.4				0.001
8				0.2				0.009
9					0.4			0.0006
10					0.2			0.008
11						0.4		0.001
12						0.2		1.0
13							0.4	0.005
14							0.2	1.0
15	0.2	0.2						0.005
16	0.2		0.2					0.003
17	0.2			0.2				0.002
18	0.2				0.2			0.0008
19	0.2					0.2		0.0005
20	0.2						0.2	0.0008
21		0.2	0.2					0.005
22		0.2		0.2				0.001
23		0.2			0.2			0.0006
24		0.2				0.2		0.0008
25		0.2					0.2	0.0011
26			0.2	0.2				0.001
27			0.2		0.2			0.0007
28			0.2			0.2		0.0009
29			0.2				0.2	0.001
30				0.2	0.2			0.0006
31				0.2			0.2	0.001
32					0.2		0.2	0.001
33						0.2	0.2	0.002

[a] Each alkynol was made by condensing sodium acetylide with the appropriate n-alkanal.

Tests were made with various concentrations of the inhibitor mixture of this invention under the severe corrosion conditions described in Table I. These tests are set out in Table II following.

TABLE II.—EFFECT OF VARIOUS CONCENTRATIONS OF THE INHIBITOR SYSTEM IN CONTROLLING ACID CORROSION

Test conditions—See Table I
Inhibitor system—1 part (by volume) heptynol + 1 part propynol

Test	Concentration inhibitor system (percent by volume)	Corrosion rate (lbs./ft.²/day)
34	0.4	0.0008
35	0.2	0.001
36	0.1	0.009

Similar results are obtained with other combinations of alkynols.

While a minimum of about 0.1% of inhibitor is required for prolonged protection at elevated temperatures of the order of 200° F., much less is effective at lower temperatures or for shorter periods. Under these milder conditions, as little as 0.01% may be adequate.

Tests were made under the same conditions as those reported in Table I using an inhibitor system composed of various ratios of one alkynol containing 3 to 6 carbon atoms combined with a second alkynol containing 7 to 10 carbon atoms. It was found that synergism occurred with volume ratios varying between 15:85 to 85:15 of the two alkynols. The most pronounced effect was observed when the alkynols were present in substantially equal amounts.

Tests similar to those described above showed that the combinations of alkynols are synergistically effective as corrosion inhibitors in aqueous solutions of other acids, including sulfuric, sulfonic, phosphoric, and acetic acid; in acids of other concentrations up to at least 50%; in acids at other temperatures up to or exceeding 200° F., depending somewhat on the identity and concentration of the acid; and in the protection of other metals, including oil field tubing, cast iron, mild steel, stainless steel, admiralty metal and copper.

Effective inhibitors are obtained by mixing three or more alkynols but in general, there is little advantage in including more than two.

Best results are obtained when the inhibitor composition comprises two alkynols differing by at least 3, and preferably 4 or 5 carbon atoms. Thus, in the preferred compositions, a lower alkynol containing 3 to 6 carbon atoms is mixed with a higher one containing about 7 to 11 carbon atoms.

We claim:

1. A corrosion inhibitor composition consisting essentially of a mixture of a pair of alkynols in a volume ratio between about 15:85 and 85:15, said pair being selected from the group consisting of

(a) propynol and butynol
(b) propynol and pentynol
(c) propynol and nonynol
(d) propynol and decynol
(e) butynol and decynol
(f) pentynol and decynol

2. A corrosion inhibitor composition consisting essentially of a synergistic mixture of propynol and butynol in the ratio of 15:85 to 85:15 by volume.

3. A corrosion inhibitor composition consisting essentially of a synergistic mixture of propynol and decynol in the ratio of 15:85 to 85:15 by volume.

4. An aqueous non-oxidizing acid containing a pair of alkynols selected from the group consisting of

(a) propynol and butynol
(b) propynol and pentynol
(c) propynol and nonynol
(d) propynol and decynol
(e) butynol and decynol
(f) pentynol and decynol

the volume ratio of the two alkynols being between about 15:85 and 85:15, said pair being present in an amount sufficient to substantially inhibit the corrosion of metals exposed to said acid.

5. A composition consisting essentially of hydrochloric acid containing about 0.01 to 0.4% by weight of a synergistic corrosion-inhibiting mixture of propynol and butynol, said mixture being in the rato of 15:85 to 85:15 by volume.

6. A composition consisting essentially of hydrochloric acid containing about 0.1 to 0.4% by weight of a synergistic corrosion-inhibiting mixture of propynol and decynol, said mixture being in the ratio of 15:85 to 85:15 by volume.

7. The process of inhibiting the corrosion of metals in contact with aqueous, non-oxidizing acid comprising incorporating into the acid a pair of alkynols selected from the group consisting of

(a) propynol and butynol
(b) propynol and pentynol
(c) propynol and nonynol
(d) propynol and decynol
(e) butynol and decynol
(f) pentynol and decynol

the volume ratio of the two alkynols being between about 15:85 and 85:15, said pair being used in an amount sufficient to substantially inhibit the corrosion of said metal.

8. The process of inhibiting the corrosion of metals in contact with hydrochloric acid comprising incorporating into the acid an effective amount of about 0.01 to 0.4% by weight, based on said acid, of an inhibitor consisting essentially of a synergistic mixture of propynol and butynol in the ratio of 15:85 to 85:15 by volume.

9. The process of inhibiting the corrosion of metals in contact with hydrochloric acid comprising incorporating into the acid an effective amount of about 0.01 to 0.4% by weight, based on said acid, of an inhibitor consisting essentially of a synergistic mixture of propynol and decynol in the ratio of 15:85 to 85:15 by volume.

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