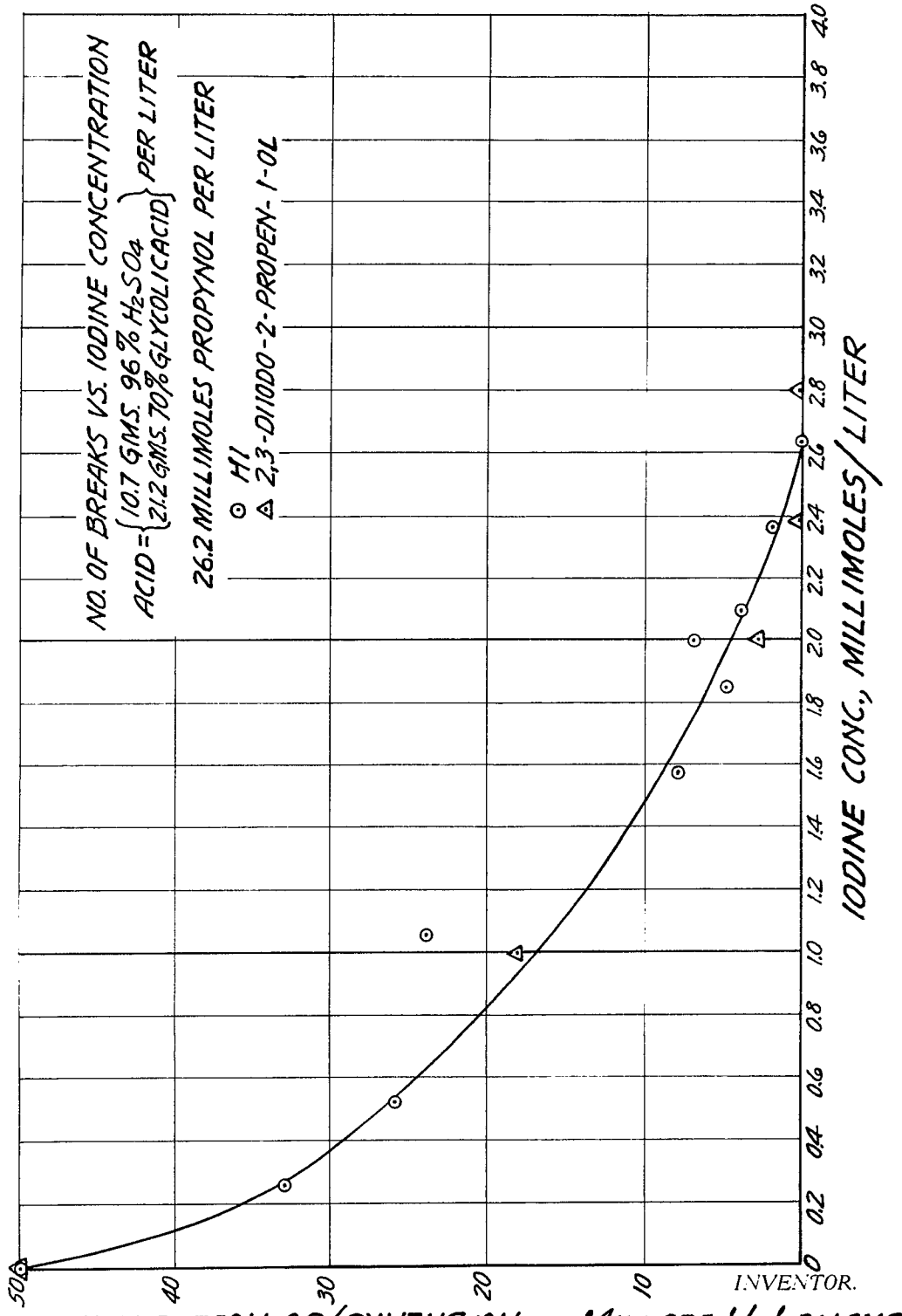
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HYDROGEN EMBRITTLEMENT PREVENTION

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HYDROGEN EMBRITTLEMENT PREVENTION

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Continuation-in-part of application Ser. No. 710,343, Mar. 4, 1968. This application Jan. 8, 1971, Ser. No. 105,122

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U.S. Cl. 252—147 8 Claims

ABSTRACT OF THE DISCLOSURE

The hydrogen embrittlement which normally occurs when high strength metal parts are immersed in acid-cleaning solution, is minimized or eliminated by adding certain combinations of (1) mono-alkynols and (2) iodine compounds which are either iodo-alkenols or suppliers of iodide ion. The molar concentrations of both alcohol and iodine compound should exceed specified threshold values.

CROSS-REFERENCE TO RELATED APPLICATION

This application is a continuation-in-part of copending application Ser. No. 710,343, filed Mar. 4, 1968 and now abandoned.

BACKGROUND OF THE INVENTION

The invention relates to a composition for minimizing or preventing hydrogen embrittlement which normally occurs during the acid cleaning of susceptible metals, especially high carbon steel.

It has long been known that when high strength metals are cleaned in acids, the phenomenon known as hydrogen embrittlement results. High carbon steel, beryllium-copper alloys, titanium, and Phosphor bronze all display this phenomenon, which is known to result when the extremely small hydrogen atom penetrates the metal. One popular theory holds that the hydrogen enters infinitesimal voids in the metal, placing the grains under three-dimensional stress and thus precluding slip or plastic movement. Regardless of the mechanism, it is known that hydrogen embrittlement can be prevented by keeping hydrogen out of the susceptible metal.

Although it is customary to include corrosion inhibitors in acid cleaning solutions, most corrosion inhibitors have little or no effect on hydrogen embrittlement; in fact, some actually aggravate the problem.

Much of the hydrogen escapes if the acid-cleaned metal is allowed to stand for extensive periods; however, if it is electroplated soon after cleaning, any residual hydrogen remains permanently entrapped and the embrittled condition continues to exist. Embrittled parts show no change in appearance and may even display excellent initial tensile strength. An insidious aspect of hydrogen embrittlement, however, is that it is both time- and stress-dependent and hence prone to cause unexpected failure when it will be most annoying or dangerous. For example, electroplated bolts used to assemble washing machines may snap several days after the machines have been crated, or an electroplated hose clamp may fail and cause loss of coolant hours after a motorist leaves the filling station where the clamp was installed. More dangerous failures may occur in the case of bolts used to assemble auto door latches, aircraft frames, etc.

A number of techniques have been developed to cope with the problem of hydrogen embrittlement. For example, an acid-cleaned part may be heated for several hours to drive off the entrapped hydrogen: although more or less effective, this treatment requires an extra operation, and the results are not uniform. Chemicals have also been included in the treating bath to prevent hydrogen embrittlement from occurring in the first place; see, for example, U.S. Pat. 3,335,089. Although such prior art additive compositions may be effective for parts formed of mild steel or other low strength alloy, they are not suitable for high strength parts.

A simple but highly reproducible test has been devised to compare the effectiveness of several acid cleaning bath additives in inhibiting hydrogen embrittlement. This test employs No. 15 spring wire hose clamps made of SAE 1065–1080 steel heat treated to a minimum Rockwell C hardness of 53. These clamps are formed from 0.121–0.123 inch wire and are designed to be used at a clamp diameter of 0.938 inch. In accordance with the test procedure used herein, 50 such hose clamps, having a total weight of about 0.72 lb. and a total area of about 89.5 square inches, are placed in 1 liter of acidic cleaning solution containing a potential hydrogen embrittlement inhibitor and heated to 75° C. while being stirred for ten minutes. The hose clamps are then removed, rinsed in tap water, dried for 1–2 minutes at room temperature and, using a standard tool designed for the purpose, immediately mounted on a rod having a diameter of 0.938 inch, thereby placing them under tensile stress. The number of hose clamps which break is noted after 24 hours.

The foregoing test is significantly more severe than any commonly employed, and ordinary acid cleaning causes all 50 clamps to break. Of the various cleaning bath additives alleged to reduce hydrogen embrittlement, the best prevent hydrogen embrittlement in, at most, a minor percentage of cases. Desirably, embrittlement should be prevented in all, or nearly all, cases.

SUMMARY

The present invention provides a novel composition which dramatically reduces or eliminates hydrogen embrittlement even in severe conditions. The invention comprises an inexpensive additive for acid-cleaning baths which makes it possible to safely clean normally embrittleable parts with strong acids. Modest amounts of additive are required to prevent hydrogen from penetrating the metal, and there is no interference with the effectiveness of the acid-cleaning operation. Even in the extraordinarily severe test alluded to above, the percentage of breakage is far less than with any treatment heretofore known. In fact, judicious selection of the ingredients used to make the novel composition can totally eliminate breakage.

In accordance with the invention, there is incorporated in a normal acid-cleaning solution specified concentrations of (1) mono-alkynol and (2) certain iodine-containing compounds. Among the mono-alkynols which have been evaluated are propynol (propargyl alcohol), butynol, pentynol, hexynol, methylbutynol, methylpentynol, ethynyl cyclohexanol, and ethyl octynol. Generally speaking, those alkynols in which the triple bond is asymmetrically located perform more effectively than those in which it is in the center of the molecule; alkynols in which the triple bond is adjacent a terminal carbon atom are particularly effective.

Suitable iodine-containing compounds are selected from the class consisting of (a) iodo-alkenols and (b) compounds which yield iodide ion in acidic solution. Among the former, a particularly preferred compound is 2,3-diiodo-2-propen-1-ol, which is a derivative formed by reacting iodine with propynol according to the following formula:

$$HC{\equiv}CCH_2OH + I_2 \longrightarrow \underset{I}{HC{=}\overset{I}{C}CH_2OH}$$

Because the iodo-alkenols are waxy and somewhat difficult to dissolve in acid solution, a surfactant is desirably included when such compounds are employed.

Among the compounds which yield iodide ion in acid solution are such soluble iodides as HI, NaI, KI, LI, $AlI_3 \cdot 6H_2O$, NH_4I, BaI_2, $CaI_2 \cdot 6H_2O$, $CoI_2 \cdot 2H_2O$, CsI, FeI_2, LaI_3, LuI_3, MgI_2, MnI_2, NdI_2, RbI, SrI_2, UI_4, VI_2, ZnI_2, CH_3I, $(CH_3)_4NI$, C_2H_5I, etc.; since these compounds are quite soluble in acid solution, it is not usually necessary to add surfactant. Soluble iodates such as HIO_3, KIO_3, $NaIO_3$, $LiIO_3$, NH_4IO_3, $La(IO_3)_3$, $MgIO_3 \cdot 4H_2O$, $Ni(IO_3)_2$, $RbIO_3$ and $Zn(IO_3)_2$ also yield iodide ion when the metallic substrate reduces the iodate ion, and can be employed. In some situations the resultant corrosion of the substrate may be objectionable, although an etched surface may be desirable for some purposes.

Although it is generally simpler to employ a single mono-alkynol and a single iodine-containing compound to produce compositions for inhibiting hydrogen embrittlement, a plurality of either or both may be employed.

In accordance with the present invention, it has been found that alkynol:iodo-alkenol blends should contain alkynol in a millimolar concentration of at least 15 (i.e., 15×10^{-3} moles per liter) and preferably at least 25, with the iodo-alkenol present in amount sufficient to provide a millimolar iodine concentration of at least 1 and preferably at least 2.5. An economically optimum diluent-free concentrate is formed from a diluent-free blend having roughly a 5:1 alkynol:iodo-alkenol molar ratio.

Alkynol:iodide blends should contain alkynol in a millimolar concentration of at least 25 and iodide compound in a millimolar concentration of at least 2 and preferably at least 2.5. An economically optimum diluent-free concentrate is formed from a diluent-free blend having roughly a 10:1 alkynol:iodide molar ratio. A blend of propargyl alcohol and HI in which the millimolar concentration of propargyl alcohol is 6.4 and that of the HI is 64 has been disclosed as a corrosion inhibitor for mild steel; see, e.g., Hackerman et al., Journal of the Electro-Chemical Society, 113, No. 7, p. 677. Such a composition, however, is essentially ineffective in inhibiting hydrogen embrittlement as measured by the test described above.

BRIEF DESCRIPTION OF THE DRAWING

The drawing is a graphical representation showing the effect of iodide or iodine concentration in preventing hydrogen embrittlement in a sulfuric-glycolic acid solution containing a fixed concentration of propargyl alcohol.

It will be appreciated, of course, that the optimum concentration of components is dependent on a number of factors, as will be now pointed out in greater detail.

THE PRESENTLY PREFERRED EMBODIMENTS

Since alkynols and iodide-yielding compounds are standard items of commerce, mutually soluble, and also dissolve in acid-cleaning solutions, blends may be prepared by simple mixing procedures. The iodo-alkenols, however, are not readily available commercially. The following paragraphs show the preparation of an iodo-alkenol and a hydrogen inhibitor concentrate.

A derivative of propynol and iodine was prepared as follows: 56.1 g. (1.0 mole) of propynol was weighed into a 1000 ml. round-bottom flask. The flask with contents was heated to 70° C. in a water bath. Using a mechanical stirrer to mix the contents of the flask, iodine crystals were added in small increments until the reaction mixture would not decolorize further, 229.6 g. (0.905 mole) of iodine crystals being required. The product was poured into an Erlenmeyer flask and solidified at room temperature to a yellowish-brown waxy mass. Analysis gave C=11.9%, H=1.3%, I=79.9% vs. theoretical for 2,3 - diiodo - 2 - propen - 1 - ol of C=11.65%, H=1.3%, I=81.9%.

The iodine-containing derivative just described may either be added to an acid cleaning solution to which an alkynol is separately added or blended with the alkynol, in which it is soluble, to form a concentrate. Where an alkynol:iodo-alkenol blend concentrate is to be formed, however, a simple procedure calls for adding iodine crystals to a stoichiometric excess of the alkynol. In any event, it is important to add sufficient surfactant to insure that the waxy iodine-containing derivatives will be solubilized in the acid cleaning solution to which the concentrate will be added. All things considered, a diluent-free concentrate containing 60% by weight of such nonionic surfactants as polyoxyethylene cetyl ether or such cationic surfactants as coco amine which is N,N-substituted with a total of 5 mols of ethylene oxide, and 40% by weight of 5.6:1 molar ratio alkynol:iodo-alkenol have proved extremely effective and economically attractive.

The tabulated list of examples below shows the comparative effectiveness of different alkynols and iodine compounds, various ratios, and concentrations of hydrogen embrittlement inhibitors in typical acid cleaning solutions. Because of the inherent variations in hose clamps, up to 5% breakage (<3 clamps out of 50) is considered acceptable.

	Acid solution, gms./liter	Mono-alkynol Type	Mono-alkynol Grams/liter	Mono-alkynol Millimoles/liter	Iodine compound Type	Iodine compound Grams/liter	Millimoles, iodine/liter	Number breaks 50 hose clamps
Example:								
Control	10.7 gms., 96% H_2SO_4; 21.2 gms., 70% glycolic acid.							50
1	do	Propynol	2.52	45	57% HI	101	450	0
2	do	do	1.47	26.2	do			50
3	do	do	1.47	26.2	do	0.06	0.263	33
4	do	do	1.47	26.2	do	0.12	0.526	26
5	do	do	1.47	26.2	do	0.24	1.052	24
6	do	do	1.47	26.2	do	0.35	1.58	8
7	do	do	1.47	26.2	do	0.41	1.84	5
8	do	do	1.47	26.2	do	0.47	2.10	4
9	do	do	1.47	26.2	do	0.53	2.36	2
10	do	do	1.47	26.2	do	0.59	2.63	0
11	do	do	1.12	20	do	0.35	1.58	12
12	do	do	1.12	20	do	0.59	2.63	5
13	do	do	1.12	20	do	0.71	3.16	5
14	do	do	0.74	13.1	do	0.35	1.58	16
15	do	do	0.74	13.1	do	0.59	2.63	22
16	do	do	0.56	10.0	do	22.4	100	34
17	do	do	0.36	6.4	do	14.4	64	37
18	do	do			do	2.24	10	50
19	do	3-butyn-2-ol	1.84	26.2	do	0.59	2.63	2
20	do	do	7.01	100	do	2.45	10	0
21	do	1-pentyn-3-ol	2.20	26.2	do	0.59	2.63	3
22	do	do	4.29	50	do	1.23	5.0	0
23	do	1-hexyn-3-ol	2.57	26.2	do	0.59	2.63	0
24	do	Methyl butynol	2.23	26.2	do	0.59	2.63	15
25	do	do	8.41	100	do	2.45	10	0
26	do	Methyl pentynol	2.57	26.2	do	0.59	2.63	11
27	do	do	9.81	100	do	2.45	10	0
28	do	Ethynl cyclohexanol	3.26	26.2	do	0.59	2.62	

TABLE—Continued

Acid solution, gms./liter	Mono-alkynol Type	Grams/liter	Millimoles/liter	Iodine compound Type	Grams/liter	Millimoles, iodine/liter	Number breaks/50 hose clamps
29 do	do	6.21	50	do	1.23	5.0	1
30 do	4-ethyl-1-octyn-3-ol	4.03	26	do	0.59	2.63	1
31 do	Propynol	1.47	26.2	KI	0.43	2.62	2
32 do	do	1.47	26.2	2,3-diiodo-2-propen-1-ol.	0.15	1.0	19
33 do	do	1.47	26.2	do	0.31	2.0	3
34 do	do	1.47	26.2	do	0.74	4.75	0
35 do	do	1.47	26.2	do	1.47	9.50	0
36 do	do	0.74	13	do	0.15	1.0	32
37 do	do	0.74	13	do	0.31	2.0	7
38 do	do	0.74	13	do	0.45	3.0	0
39 do	3-butyn-2-ol	3.37	52.8	3, 4-diiodo-3-buten-2-ol.	3.45	17.2	1
40 do	1-pentyn-3-ol	4.39	52.1	1, 2-diiodo-1-penten-3-ol.	3.19	19.6	0
Control 104.2 gms., 96% H_2SO_4							50
41 do	Propynol	3.93	70	KI	1.17	7.0	0
42 do	do	3.06	54.6	do	0.33	2.0	20
43 do	do	3.06	54.6	do	0.91	5.46	11
44 do	do	3.93	70	NaI	1.05	7.0	1
45 do	do	3.93	70	KIO_3	1.50	7.0	0
46 do	do	3.93	70	$(CH_3)_4NI$	1.41	7.0	0
47 do	do	0.74	13	2,3-diiodo-2-propen-1-ol.	0.45	2.90	36
48 do	do	2.0	35.6	do	2.0	13.0	0
49 do	do	3.06	54.6	57% HI	0.45	2.0	16
50 do	do	3.06	54.6	do	0.90	4.0	0
51 do	do	3.06	54.6	do	1.12	5.0	0
52 do	do	3.06	54.6	do	1.35	6.0	2
53 do	do	2.94	52.4	do	0.67	3.0	0
54 do	do	2.94	52.4	do	1.18	5.3	2
55 do	do	2.94	52.4	do	1.35	6.0	1
56 do	do	2.52	45	do	0.17	0.8	47
57 do	do	2.52	45	do	0.34	1.5	31
58 do	do	2.52	45	do	0.45	2.0	26
59 do	do	2.52	45	do	0.68	3.0	10
60 do	do	2.52	45	do	1.01	4.5	1
61 do	do	2.52	45	do	1.18	5.3	3
62 do	do	2.52	45	do	1.35	6.0	8
63 do	do	3.06	54.6	CH_3I	0.71	5.0	32
64 do	do	3.06	54.6	C_2H_5I	0.71	5.0	18
65 do	do	3.06	54.6	C_2H_5I	2.34	15.0	2
66 52.1 gms., 96% H_2SO_4	do	2.94	52.4	C_2H_5I	1.18	5.3	0
Control 100 gms., sulfamic acid							50
67 do	Propynol	3.92	70	57% HI	1.57	7.0	0
Control 286 gms., 35% HCl							50
68 do	Propynol	1.47	26.2				50
69 do	do	2.94	52	57% HI	0.22	0.9	13
70 do	do	2.94	52	do	0.44	1.81	16
71 do	do	2.94	52	do	0.59	2.63	1
Control 29.4 gms., 85% H_3PO_4							50
72 do	Propynol	1.47	26.2	57% HI	0.59	2.63	23
73 do	do	5.61	100	do	2.45	10.0	3

What is claimed is:

1. As a new composition of mattter having particular utility for decreasing the hydrogen embrittlement of high-carbon steel parts in acid-cleaning solutions, a concentrated liquid solution consisting essentially of

(1) a mono-alkynol and

(2) at least one iodine-containing compound selected from the class consisting of

(a) iodo-lower alkenols,

(b) iodides soluble in said acid, and

(c) inorganic iodates soluble in said acid,

the mole ratio of (1):(2) being about 5:1 when the iodine-containing compound is an iodo-alkenol and about 10:1 when the iodine-containing compound is an iodide or iodate.

2. The composition of claim 1 wherein the triple bond of the mono-alkynol is asymmetrically located in the carbon chain.

3. The composition of claim 2 wherein the mono-alkynol is propargyl alcohol.

4. The composition of claim 3 wherein the iodine-containing compound is 2,3-diiodo-2-propen-1-ol.

5. As a new composition of matter, an aqueous solution having particular utility for cleaning and descaling high-carbon steel parts without imparting hydrogen embrittlement thereto, said solution consisting essentially of a strong acid in concentration adequate to clean and descale high-carbon steel parts and normally impart hydrogen embrittlement thereto, and an effective amount of a hydrogen embrittlement suppressant consisting essentially of

(1) at least about 15 millimoles of mono-alkynol per liter,

(2) sufficient iodio-lower alkenol to provide at least about 2 millimoles of iodine per liter, and

(3) sufficient surfactant to solubilize said iodo-lower alkenol in said solution.

6. The solution of claim 5 wherein the mono-alkynol is propynol and the iodo-alkenol is 2,3-diiodo-2-propen-1-ol, the former being present at a concentration of at least 25 millimoles per liter and the latter at a concentration of at least 25 millimoles per liter.

7. As a new composition of matter, an aqueous solution having particular utility for cleaning and descaling high-carbon steel parts without imparting hydrogen embrittlement thereto, said solution consisting essentially of in combination a strong acid in concentration adequate to clean and descale high-carbon steel parts and normally impart hydrogen embrittlement thereto, and an effective amount of a hydrogen embrittlement suppressant consisting essentially of

(1) at least 25 millimoles of mono-alkynol per liter, and

(2) sufficient iodides soluble in said acid to provide at least 2.5 millimoles of iodine per liter.

8. The method of reducing the normal tendency of an acidic cleaning solution to embrittle metal parts such as high strength steel, comprising adding to said solution:

(1) a mono-alkylnol ,and

(2) at least one iodine-containing compound selected from the class consisting of

(a) iodo-lower alkenols,

(b) iodides soluble in said acid, and

(c) inorganic iodates soluble in said acid,

the additives being selected in amount such that if iodo-lower alkenol is employed the concentration of mono-

alkynol is at least 15 millimoles per liter and the concentration of iodine-containing compound is at least 2 millimoles per liter, and if the only iodine-containing compound is soluble iodide or iodate, the concentration of mono-alkynol is at least 25 millimoles per liter and the concentration of hydriodic acid is at least 2.5 millimoles per liter.

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CERTIFICATE OF CORRECTION

Patent No. 3,686,129 **Dated** August 22, 1972

Inventor(s) Loucks

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 3 and 4, in the Table, under "Mono-alkynol Grams/liter", Example 22, "4.29" should be -- 4.20 --

Signed and sealed this 20th day of February 1973.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents

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