



REG. U. S. PAT. OFF.

HYDROXYACETIC ACID

70% SOLUTION — TECHNICAL

ACTIVE INGREDIENT:

Hydroxyacetic acid (Glycolic acid) 70%

INERT INGREDIENTS 30%

ACCEPTED
Oct - 20, 1972
UNDER THE FEDERAL INSECTICIDE
FUNGICIDE AND RODENTICIDE ACT
FOR ECONOMIC POISON REGISTER
ED UNDER NO. *352-309*

EPA Reg. No. 352-304-AA

Keep out of reach of children.

**DANGER! MAY CAUSE BURNS OR DAMAGE TO THE EYES.
MAY BE HARMFUL OR FATAL IF SWALLOWED.**

Do not get in eyes, on skin, or on clothing.

In case of contact, immediately flush eyes or skin with plenty of water for at least 15 minutes; for eyes, call a physician.

FIRST AID — If swallowed, drink milk, raw egg white, mucilage or gelatin solution; if these are not available drink large quantities of water. Call a physician.

FOR TECHNICAL AND USE INFORMATION, SEE DU PONT BULLETINS.

Do not reuse drum; destroy by perforating or crushing and burying in a safe place.

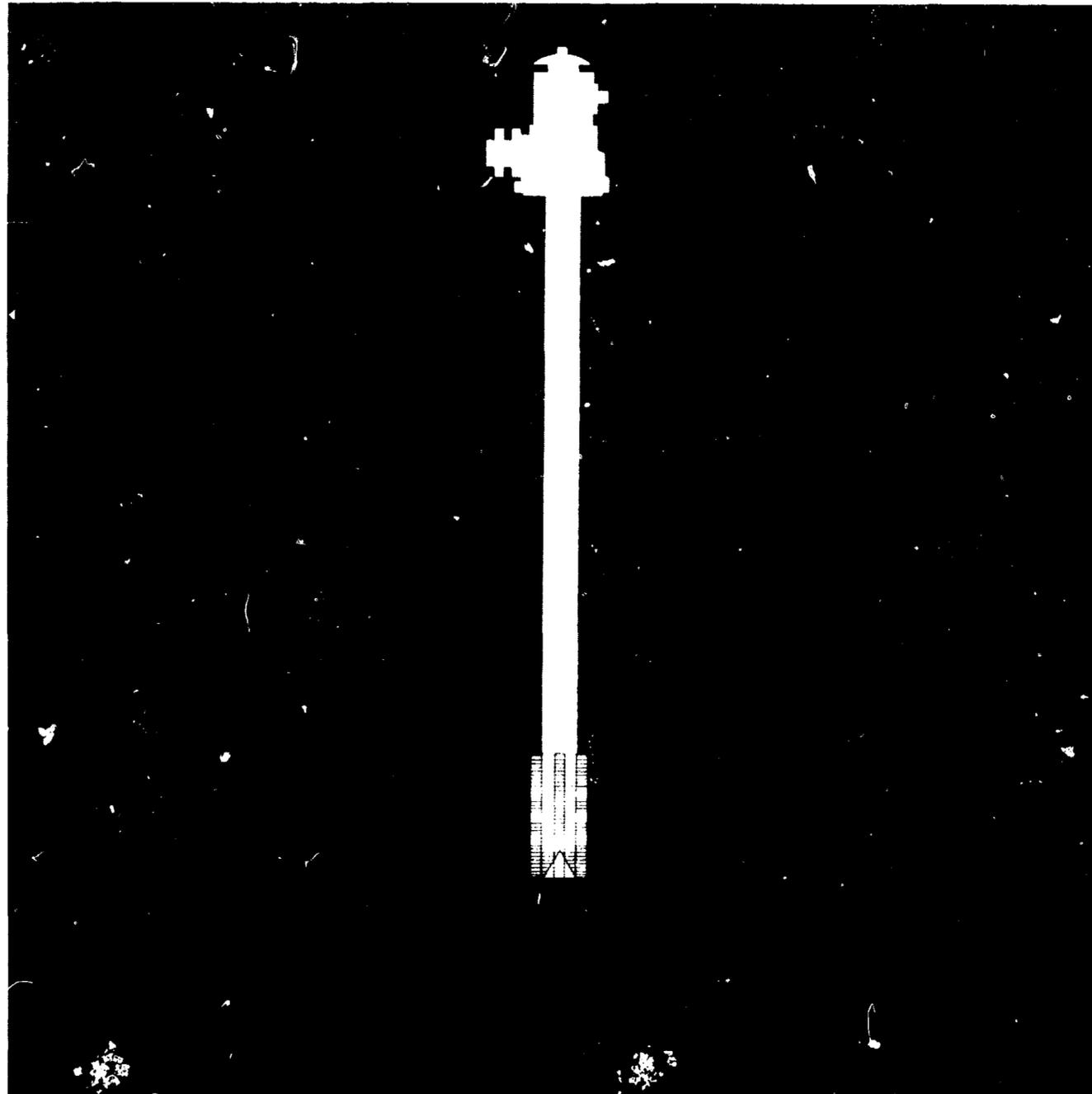
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IC-18160 5-72

MADE IN U.S.A.
PRINTED IN U.S.A.

E. I. DU PONT DE NEMOURS & CO. (INC.), INDUSTRIAL CHEMICALS DEPARTMENT, WILMINGTON, DEL.

WATER WELL STIMULATION WITH DU PONT HYDROXYACETIC AND SULFAMIC ACIDS



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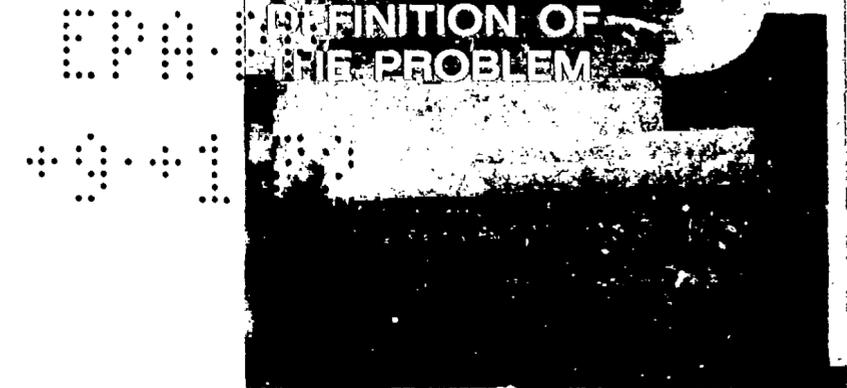
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EPA AND AGRICULTURE
ED. 352-304

INTRODUCTION



Chemical cleaning of water wells to restore or increase productivity has become accepted practice in recent years. Acid cleaners are generally the most effective agents to remove encrusting materials on metal screens, pump parts, and from pores of underground water-bearing formation. The purpose of this bulletin is to acquaint well owners, drillers, cleaning contractors and formulators of well cleaning agents with hydroxyacetic acid and sulfamic acid, two Du Pont products which are particularly suitable for use in water well stimulation. This information also is offered as a guide to the user in selection of the proper Du Pont chemical agent for treatment of problem wells.

Successful acidizing of water wells is not simple, due largely to the difficulty in defining the actual cause of capacity decrease in a given well. These causes vary widely with geographical location. Each well must be analyzed as a separate and distinct case. On the following pages, some of the more important considerations and approaches to successful well stimulation are summarized.



DEFINITION OF THE PROBLEM

CAUSES OF WELL PLUGGAGE

Reduction of well output can be caused by one or more conditions. Among the most common are the following.

1. Precipitation of calcium and/or magnesium carbonates in the strata, on well screens or in pump and discharge lines due to high water alkalinity.
2. "Air dewatering" of the screen and surrounding formation, resulting from serious drawdown of water level. This can lead to precipitation of metal salts and hydroxides of iron, calcium and magnesium in strata and screen pores.
3. Deposition of clay or silt from either sagging strata or gradual buildup in and around the pump screen.
4. Slime formation caused by iron bacteria, such as *Crenothrix*, *Leptothrix*, *Clonothrix*, and sulfate-reducing bacteria *Desulfovibrio desulfuricans*, and the iron-oxide excreting *Gallionella ferruginea*. Hydroxyacetic acid has been proven to be particularly effective against *Gallionella*, which is a frequent cause of well plugging.
5. Slime formation caused by other types of organisms. Certain bacteria, by either altering environmental conditions or by utilizing a portion of the manganese radical present in plant life upon which they feed will deposit large quantities of manganese. By subsequent bacterial action, the manganese may eventually be precipitated as manganese carbonate or manganese hydroxide.

Other possible causes of reduced output which are not related specifically to pluggage are drops in water tables or reduced pump efficiency due to wear and age.

In order to choose the most effective cleaning method, as much of the following well history as possible should be determined.

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Well History

Age of well, depth, water table level, materials of construction (see page 5); history of past cleanings, if any; types of agents used, how applied, and results.

Specific Capacity History

Specific capacity, or gallons per minute (gpm) per foot of drawdown, is a term commonly used to describe well output as related to water level under static versus dynamic conditions.

Decreasing specific capacity is an indication of well fouling.

Example:

$$\text{Specific Capacity} = \frac{\text{Flow Rate}}{\text{Drawdown}}$$

Flow Rate = 800 gpm

Distance from ground to water level when not pumping = 80 ft. (static)

Distance from ground to water level while pumping = 100 ft. (dynamic)

Drawdown = 100-80 = 20 ft.

Specific Capacity = $\frac{800}{20}$ = 40 gpm/ft. drawdown

Water Analysis

Water analysis should include where possible, level of pH, alkalinity, iron, manganese and certain bacteria.

pH in the 7.5-and-above range, showing total carbonates in the 300-to-700 ppm range, indicates a probability of heavy carbonate scales. Carbonates in the 50-to-300 ppm range indicate moderate to heavy scales. Fifty ppm or less of carbonates indicates light to moderate scale buildup.

Ferric hydroxide can be present throughout the range of pH normally found in well waters. Soluble iron in

the 5-to-10 ppm range is considered a relatively high iron level and indicates the probability of high iron scale. When this condition exists, the possible presence of iron bacteria should be investigated. It has been reported that many bacteria act upon solutions of less than 0.5 ppm of iron. Low iron is no certainty of absence of iron bacteria.

Reports on Manganese Deposits in Western Reservoirs and Distribution Systems (H. C. Myers, California Water & Telephone Company, 1960) indicated slime problems occurred with manganese levels as low as 0.1 ppm.

Scale Analysis

Frequently, analyses of scales removed from pump parts or screens may show clearer evidence of the problem than the often-delicate water analysis, where very low levels of constituents may not be detectable. This is sometimes true in the case of sheathed iron bacteria which are often encapsulated by iron scales.

Detection of Bacteria

Detection of bacteria usually is the most difficult to accomplish.³ Screening of water through membrane filters or careful and prompt analyses of water, mud or iron scale samples by a qualified laboratory assists in identification of iron bacteria.

Figures 1, 2 and 3 show plate photographs, reproduced from an article by J. M. Sharpley entitled "Bacteria in Flood Water: What They Are, What They Mean" (PETROLEUM ENGINEER, February 1961). Mr. Sharpley reported that "... characteristically, Gallionella is found in large numbers in water containing fair amounts of carbonic acid after penetrating iron-containing geologic strata." "Another characteristic place to find Gallionella is in source wells utilizing water from either river gravel beds or old glacial fills. As an illustration of these two sources of Gallionella, the water from the alluvial gravel adjacent to the Arkansas River and fresh

water wells drilled in the Wabash Valley basin . . . have been found to contain Gallionella in large numbers."

MATERIALS OF CONSTRUCTION

Materials used for screen construction vary widely. Copper, stainless steel, "Everdur", red brass, galvanized steel, nickel and mild steel are among the most common. Pump parts and lines may be mild steel, black iron, cast iron, galvanized steel or stainless steel. Concrete is used often for casement construction.

The foregoing points out most clearly the importance of selecting a cleaning agent which will have minimal effect upon expensive well components by corrosive action. Hydroxyacetic and sulfamic acids normally meet this need, while at the same time providing effective well cleaning action.

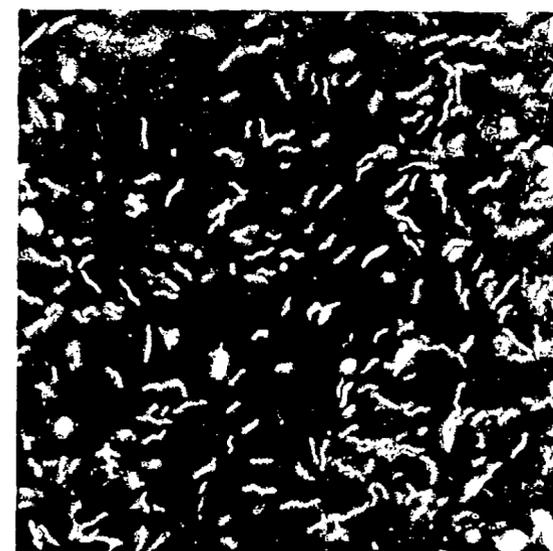


FIG. 1. Sulfate-reducing bacteria in connate water. The white cells are shown against a dark contrasting background. Sulfates are reduced to hydrogen sulfide.



FIG. 2. Sphaerotilus sheathed iron bacteria, forming slime on a corrosion coupon. They occur in lines rather than in tanks or filters.



FIG. 3. Another species of iron bacteria, Gallionella, excretes long, twisted strands of iron oxide. The microorganism itself is rarely seen except by special cultural techniques.

*American Brass Company registered trademark

COMMONLY USED TREATING AGENTS 2

Some of the more commonly-employed agents for well stimulation are listed below.

Hydroxyacetic Acid²—Chelates and removes light iron and carbonate scales, controls *Gallionella* iron bacteria and inhibits their further regrowth. (See Section 3.)

Sulfamic Acid^{1,7}—Removes carbonate scales and light iron scales effectively, while minimizing corrosion to expensive equipment. (See Section 3.)

H.T.H.—Calcium Hypochlorite 70%^{3,4}—For water purification. Common household bleaches sometimes also are used.

Inhibited Hydrochloric Acid^{1,3,7}—Removes heavy iron oxide, sulfide and carbonate scales. Care must be exercised to minimize corrosion of equipment and avoid precipitation of ferric hydroxide upon dilution. To prevent the latter possibility, chelating agents are frequently used in conjunction with hydrochloric acid.

Chelating Agents¹—Tartaric acid, citric acid, ethylenediamine-tetracetic acid and other agents are used for iron chelation in combinations with HCl or alone.

Sodium Hexametaphosphate—Used frequently before acid treatment to break up and float out clays and silt. Concentrations of 25-to-30 lb. per 100 gal. of water generally are used, followed by vigorous surging. (Not recommended where calcium levels are high, due to insolubility of calcium phosphates.)

Details on the use of hydroxyacetic acid and sulfamic acid appear later in this bulletin. With regard to the use of the other chemicals listed above, the manufacturer's or distributor's directions regarding their use in water wells should be strictly followed.

ADVANTAGES OF DU PONT ACIDS 3

HYDROXYACETIC ACID

A 70% solution of hydroxyacetic acid is a particularly advantageous agent for well stimulation for the following reasons.

Effective anti-bacterial action—controls the *Gallionella* iron bacteria which causes precipitation of iron oxide. This material not only plugs well strata and screens but also can cause pit-type corrosion.

Effective bacteriostat—inhibits the growth of many bacteria.

Effective chelating agent—particularly for iron, and to a lesser extent for calcium and magnesium (it ties them up in soluble form so they can be pumped from the well).

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Safer for equipment—very mildly corrosive and safe on all well metals.

Sulfamic acid is a dry, white, granular or crystalline acid. It is a strong inorganic acid, yet only mildly corrosive.

Effective and rapid carbonate removal—most salts of sulfamic acid are more soluble than corresponding chloride, sulfate or nitrate salts.

Effective for light iron oxide removal—it can be mixed with common salt for very tough iron scales.

Rapid solubility in water—up to 18% at 70°F.

Dry, easy to handle—one 400-lb. fiber drum is equivalent in acidizing power to seven 13-gallon carboys of 20% hydrochloric acid. It can be added to the well either in solution or dry form.

Safer for equipment—has low corrosion rates on metals. Does not cause stress cracking on stainless steel. Can also be used in contact with certain plastics such as baked phenolics, polyethylene, reinforced epoxies and polyvinylchloride.

Many problem wells must be treated either with a mixture of acids, or in sequence with different acids to remove pluggage effectively. Du Pont hydroxyacetic and sulfamic acids can be blended to provide an effective cleaning agent for many conditions. In some instances, use of inhibited hydrochloric acid^{1,3,7} will be desirable where especially tough measures are called for.

CHOOSING THE PROPER AGENT



SELECTION GUIDELINES

Selection of the proper agent or combination of agents, based on previously collected data and well history is the key to successful application.

The following guidelines will be helpful in making this selection.

1. Where light iron scale and iron bacteria are present, use hydroxyacetic acid.
2. Where carbonate scale and iron bacteria are present, use a mixture of hydroxyacetic acid and sulfamic acid.
3. Where very heavy carbonate scale and iron bacteria are present, use a combination of hydroxyacetic acid with either sulfamic acid or hydrochloric acid.
4. Where heavy iron and heavy carbonate scales are present and a dry acid descaler is preferred, use a mixture of sulfamic acid and sodium chloride.

5. Where moderate iron and carbonate scales are present, use sulfamic acid alone.

ADDITIONAL FORMULATION

Du Pont acids, either alone or in combination, offer a solution to many types of well pluggage. Three liquid and two dry formulations are suggested in Tables I and II.

USE OF CORROSION INHIBITORS AND WETTING AGENTS

At the lower temperatures encountered in well cleaning, the use of inhibitors for either sulfamic or hydroxyacetic acid usually is not necessary. However, occasionally in old wells the encrustation buildup can be so severe that the scale covering the pump parts may actually become part of the bearing surfaces. Consequently, following an effective acid cleaning, pump parts may no longer be tight fitting,

TABLE I.
SUGGESTED LIQUID FORMULATIONS BASED ON
DU PONT HYDROXYACETIC-SULFAMIC-HYDROCHLORIC ACIDS

Formulation	Problem		
	A	B	C
	<ul style="list-style-type: none"> ● Light-to-moderate iron scale ● Iron bacteria ● Light carbonate scale 	<ul style="list-style-type: none"> ● Heavy iron scale ● Iron bacteria ● Light-to-medium carbonate scale 	<ul style="list-style-type: none"> ● Heavy carbonate scale ● Iron bacteria ● Medium iron scale
Hydroxyacetic Acid (70% Tech), %	98	70	30
Sulfamic Acid, %	—	10	—
Inhibited Hydrochloric Acid, %	—	—	63
"Merpol" ^a OE, %	2	2	2
Water, %	—	18	5
	100	100	100

a. Du Pont registered trademark for its surface active agents

with a resulting decrease in pump efficiency. This is not unlike boiler cleaning, wherein scale develops in tubes following removal of scale from badly corroded areas, leading to the erroneous conclusion that the cleaning agent caused the condition. For this reason, and as a matter of additional safety, most formulators include inhibitors in their mixtures. In any event, the decision on use of inhibitors should be contingent on the specific circumstances encountered.

Use of wetting agents is considered good practice to improve cleaning performance; therefore, they

have been included in the suggested formulations.

Many wetting agents and corrosion inhibitors are toxic in nature. Therefore, it is suggested that where they are used in cleaning formulations, State agencies should be advised as to concentration and type being used. In States where required, it is good practice to have available analyses of the well water both prior to treatment and after flushing, to determine residual level of inhibitor concentration.

A number of compatible corrosion inhibitors and wetting agents are listed in Table III.

TABLE II.
SUGGESTED DRY FORMULATIONS BASED ON DU PONT SULFAMIC ACID

Formulation	Problem	
	A	B
	<ul style="list-style-type: none"> ● Heavy Iron Scale ● Slight Carbonate Scale ● No Bacteria 	<ul style="list-style-type: none"> ● Moderate Iron Scale ● Moderate Carbonate Scale ● No Bacteria
Sulfamic Acid, %	65.0	95.0
Salt (NaCl), %	30.0	—
"Pluronic" ^a F-68-LF, %	2.5	2.5
"Rodine" ^b 115, %	2.5	2.5
	100.0	100.0

a. Amchem Products, Inc., registered trademark.
b. Wyandotte Chemicals Corporation registered trademark.

TABLE III.
SUGGESTED WETTING AGENTS AND CORROSION INHIBITORS
FOR USE WITH SULFAMIC AND HYDROXYACETIC ACIDS^a

Wetting Agents (All Concentrations 2 Lb. Agent/100 Lb. Acid)^b

Wetting Agent	Characteristics	Form
"Pluronic" F-68-LF	Low foaming; non-ionic	Solid
"Merpol" OE	Low foaming; non-ionic	Liquid
"Triton" ^c X-100	Non-ionic	Liquid
"Renex" ^d 35	Non-ionic	Solid

NOTE: Anionic wetting agents may be precipitated by certain inhibitors in acid solutions; therefore, only the non-ionic type are listed here.

Inhibitors for Sulfamic Acid

Inhibitor	Concentration (Lb./100 Lb. Acid)	Form
"Aldac" ^e 97	2	Powder

The following are particularly good for copper, brass, 304 and 316 stainless steel:

Inhibitor	Concentration (Lb./100 Lb. Acid)	Form
"Rodine" 115	1	Brown Powder
"Rodine" 140	7	Off-white Powder
("Rodine" 140 is also effective on galvanized steel)		
"Ferrifloc" ^f —Hydrated Ferric Sulfate (For stainless steel)	1	Off-white Powder

a. These wetting agents and inhibitors are some which have been tested with these acids. There is no intent to imply that they are the only ones acceptable.
b. Calculated on total acid content of formula.

c. Rohm & Haas Company registered trademark.
d. Atlas Chemical Industries, Inc., registered trademark.
e. Aldoa Chemical Company registered trademark.
f. Tennessee Corporation registered trademark.

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Selection of the proper agent or combination of agents based on previously collected data and well history is the key to successful application.

The following guidelines will be helpful in making this selection:

1. Where light iron scale and iron bacteria are present, use hydroxyacetic acid.
2. Where carbonate scale and iron bacteria are present, use a mixture of hydroxyacetic acid and sulfamic acid.
3. Where very heavy carbonate scale and iron bacteria are present, use a combination of hydroxyacetic acid with either sulfuric acid or hydrochloric acid.
4. Where heavy iron and heavy carbonate scales are present and a dry acid solution is preferred, use a mixture of sulfamic acid and sodium chloride.

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Hydroxyacetic Acid (70% Tech), %	98	70	30
Sulfamic Acid, %	--	10	--
Inhibited Hydrochloric Acid, %	--	--	63
"Merpol" OE, %	2	2	2
Water, %	--	18	5
	100	100	100

5. Where moderate iron and carbonate scales are present, use sulfamic acid alone.

Du Pont acids, either alone or in combination, offer a solution to many types of well pluggage. Three liquid and two dry formulations are suggested in Tables I and II.

At the lower temperatures encountered in well cleaning, the use of inhibitors for either sulfamic or hydroxyacetic acid usually is not necessary. However, occasionally in old wells, the encrustation buildup can be so severe that the scale covering the pump parts may actually become part of the bearing surfaces. Consequently, following an effective acid cleaning, pump parts may no longer be tight fitting,

with a resulting decrease in pump efficiency. This is not unlike isotherm cleaning where in that, that develops in tubes following removal of scale from badly corroded or plugged wells, to the iron bacteria conclusion that the chlorine agent causes the formation of the bacteria and the formation of hydroxyacetic acid most favorable to the inhibitor in the reaction. In any event, the development of pluggage should be controlled by the proper inhibitor usage to be countered.

Use of wetting agents is considered necessary to improve cleaning performance. The following

have been included in the suggested formulations.

Many wetting agents and corrosion inhibitors are toxic in nature. Therefore, it is suggested that water dilutions and low concentration formulations be used. Where possible, use of inhibitors in acid solutions should be adjusted to the well water conditions to be treated and not to the high acid concentrations which would inhibit the formulation.

Formulations of compatible corrosion inhibitors for use with acids are listed in Table III.

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SUGGESTED DRY FORMULATIONS BASED ON DU PONT SULFAMIC ACID

Formulation	Problem	
	A	B
	<ul style="list-style-type: none"> • Heavy Iron Scale • Slight Carbonate Scale • No Bacteria 	<ul style="list-style-type: none"> • Moderate Iron Scale • Moderate Carbonate Scale • No Bacteria
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Salt (NaCl), %	30.0	--
"Pluronic" F-68-LF, %	2.5	2.5
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2 Lb. Agent/100 Lb. Acid)^a

"Pluronic" F-68-LF	Low foaming: non-ionic	Solid
"Merpol" OE	Low foaming: non-ionic	Liquid
"Triton" X-100	Non-ionic	Liquid
"Renex" 35	Non-ionic	Solid

NOTE: Anionic wetting agents may be precipitated by certain inhibitors in acid solutions; therefore, only the non-ionic type are listed here.

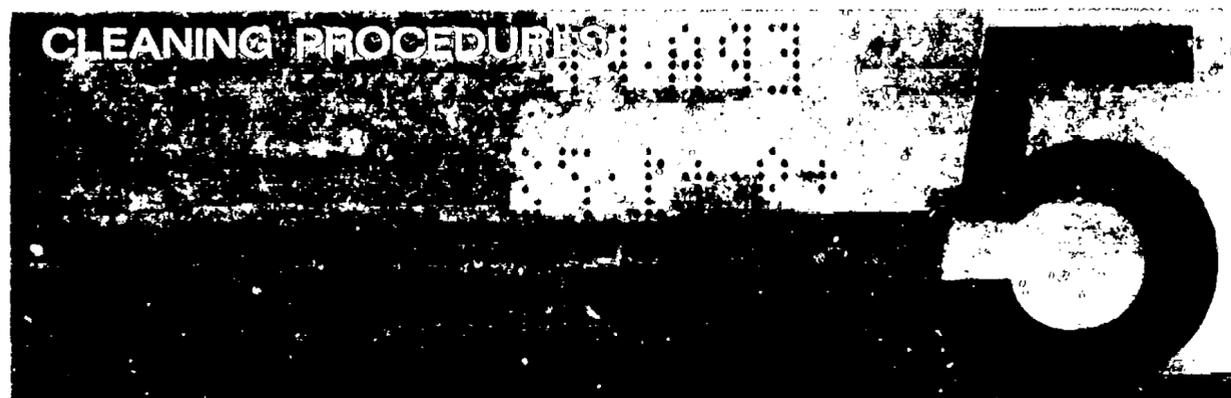
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Concentration (Lb./100 Lb. Acid)

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The following are particularly good for copper, brass, 304 and 316 stainless steel:		
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("Rodine" 140 is also effective on galvanized steel)		
"Ferrifloc" Hydrated Ferric Sulfate (For stainless steel)	1	Off white powder

^a These wetting agents are listed here as they are used in acid solutions. There are many other types of wetting agents available, but only these are listed here as they are the only ones which are compatible with acids.

^b These corrosion inhibitors are listed here as they are used in acid solutions. There are many other types of corrosion inhibitors available, but only these are listed here as they are the only ones which are compatible with acids.



After an analysis of well conditions is completed and choice of chemicals is made, the following procedures are recommended.

Under normal conditions, an acid concentration is employed (calculated as 100% acid) in the range of 5 to 10 percent in the cleaning solution, based on the volume of water determined from the static water level in the well. It should be recognized that in many instances, particularly where bacteria or heavy scales are present, serious pluggage may be

present in the strata as well as in the pump screen itself. In heavy bacteria situations, acid concentrations as high as 20 percent, based on the static head, may be required to give a 5 to 10 percent concentration several feet out into the surrounding strata. Successful cleanings have been achieved using such an approach.

Table IV is a quantity guide for 5 percent concentrations of either hydroxyacetic or sulfamic acid, which are considered absolute minimum requirements. These figures may be factored to calculate

**TABLE IV.
QUANTITY GUIDE — HYDROXYACETIC ACID AND SULFAMIC ACID
FOR CLEANING WATER WELLS**

Diameter of Well in Inches	Pounds of Dry Sulfamic Acid to Add per Foot of Water to Give a 5% Solution	Gallons of Hydroxyacetic Acid 70% to Add per Foot of Water to Give a 5% Solution
2	0.07	0.010
4	0.28	0.040
6	0.63	0.090
8	1.02	0.160
10	1.75	0.241
12	2.50	0.361
14	3.08	0.491
16	3.78	0.641
18	5.67	0.811
20	7.00	1.000
22	8.47	1.210
24	10.00	1.440
26	10.83	1.690
28	13.72	1.960
30	15.75	2.250

Example: A 10-inch diameter well 126 feet deep with a static water level 30 feet below the surface would require: $(126 - 30) \times 0.241 = 23.1$ gallons of hydroxyacetic acid 70% solution technical.

Example: A 12-inch diameter well 100 feet deep with a static water level 25 feet below the surface would require: $(100 - 25) \times 2.5 = 187.5$ pounds of dry sulfamic acid.

required amounts for higher dosages or usages of mixtures.

INTRODUCTION OF CHEMICALS

The most effective method of chemical introduction is by separate pipe directly to the inside of the screen area. Where this is not possible, chemicals may be introduced through the pump discharge line or well casing, from the surface, using surging as required to disperse the necessary quantity.

Delivery of chemicals directly to the screen area is becoming an increasingly recognized necessity and many new wells are constructed with facilities for doing so. Where opportunities arise in cleaning or repair of existing wells, consideration should be given to adding such facilities to simplify subsequent

cleaning operations. Introduction of chemicals back through the well casing or pump suction of old wells may result in poor delivery of chemicals to proper areas, with subsequent mediocre cleaning success.

After adding the acid, use a surge-block, or back-flush the well with water from another source in order to facilitate mixing and to achieve penetration into the well formation.

Acid treating times should range from a minimum of 24 hours to 48 hours total contact. By starting and stopping the pump, surge the column of water to the

top of the well every 3 or 4 hours or oftener to help dislodge scale. Where heavy scale deposits are encountered, effluent acidity should be checked periodically by either pH measurement or titrating to insure sufficiency of acid to complete the cleaning job. If pH is above 2, or total acidity below 0.1%, repeat treating is indicated and additional cleaning agent should be added.

Sequential treatment may sometimes be required to first remove substrate scale (HCl or sulfamic acid), followed by hydroxyacetic acid for effective bacteria control. A condition of very high scale and *Gallionella* count could be such a case.

Pump the water to waste, slowly at first and then at about 25 percent of full flow. At 15-to-30 minute intervals, stop the pump long enough to allow the well to regain its static level; this procedure aids in keeping any solid matter suspended.

Continue pumping to waste until the pH of the water is within 0.5 pH unit of the original value before treatment. A commercial pH meter, such as Beckman Model G or equivalent may be used. These values are usually achieved within 1 to 3 hours after starting the flushing operation.

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After an analysis of well conditions is completed and choice of chemical is made, the following procedures are recommended:

Under normal conditions, an acid concentration is employed calculated as 100% acid in the range of 5 to 10 percent in the cleaning solution, based on the volume of water determined from the static water level in the well. It should be recognized that in many instances, particularly where bacteria or heavy scales are present, serious pluggage may be

present in the strata as well as in the pump screen itself. In heavy bacteria situations, acid concentrations as high as 20 percent, based on the static head, may be required to give a 5 to 10 percent concentration several feet out into the surrounding strata. Successful cleanings have been achieved using such an approach.

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6	0.63	0.090
8	1.02	0.160
10	1.75	0.241
12	2.50	0.361
14	3.08	0.491
16	3.78	0.641
18	5.67	0.811
20	7.00	1.000
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The most effective method of chemical introduction is by separate pipe directly to the inside of the screen area. Where this is not possible, chemicals may be introduced through the pump discharge line or well casing from the surface, using stirring as required to disperse the necessary quantity.

Delivery of chemicals directly to the screen area is becoming an increasingly recognized necessity and many new wells are constructed with facilities for doing so. Where opportunities arise in cleaning or repair of existing wells, consideration should be given to adding such facilities to simplify subsequent

cleaning operations. Introduction of chemicals back through the well casing or pump suction of old wells may result in poor delivery of chemicals to proper areas, with subsequent ineffective cleaning.

After adding the acid, use a sample block or pump flow the well with water from another source in order to facilitate movement of acid down into the well formation.

Acid treatment should be kept from a maximum of 24 hours to 48 hours total contact. By starting and returning the pump to the column of water to the

top of the well every 2 or 4 hours, an attempt may be made to disperse scale. Where heavy scale deposits are encountered, sufficient acidity should be checked periodically by either pH measurement or titration to insure sufficiency of acid to complete the cleaning. If pH is above 2 or total acidity below 0.1%, repeat treatment is indicated, and additional cleaning agent should be added.

Sequential treatment may sometimes be required to first remove substrate scale (HCl or sulfamic acid) followed by hydroxyacetic acid for effective bacteria control. A condition of very high scale and Gallinella count could be such a case.

Pump the water to water level of treatment and acid 20 percent of run flow. At the end of treatment, stop the pump long enough to allow the water to return to static head. The procedure is then repeated if further cleaning is needed.

Constant pumping to water level of treatment with water of pH up to 3.0 or 4.0 is suggested for 24 hours. A sample of water should be taken after 24 hours. Microbiological testing may be required to determine if any additional treatment is necessary.

ADDITIONAL SUGGESTIONS

6

FOLLOW UP ON PERFORMANCE

Accurate records on specific capacity and occasional analysis for bacteria should be maintained to insure adequate measurement of cleaning performance and retained well efficiency. Some authorities suggest that cleaning should be instigated or repeated no later than when specific capacity has dropped to 75 percent of original performance, followed by routine cleanings at least once per year.

SEEDING OF WELLS AND TREATMENT

One danger exists which is recognized by those who drill wells, but is frequently overlooked by those who only occasionally clean them. This problem is referred to as "bacteriological seeding of wells" and occurs by contamination of previously clean water tables from tools and other equipment used in drilling or cleaning operations.

Where hydroxyacetic acid has not been employed as the cleaning agent, recommended practice is to treat the well with calcium hypochlorite at a rate of 1 or 2 pounds per 100 gallons of water at static level in the well, surging as required to adequately effect dispersion.

STORAGE AND HANDLING

7

Du Pont hydroxyacetic acid 70% solution is available in bulk in lined tank cars and tank trucks and in lined 55-gallon drums. It freezes at 50°F and should be protected from cold weather. If frozen, it can be thawed out and used following thorough mixing.

Du Pont sulfamic acid is available in two forms—Sulfamic Acid Crystal Technical (crystalline, 99% pure) and Sulfamic Acid Granular Technical (granular, 93% pure). Although either form may be used, the granular form is recommended due to its more free flowing and slightly faster solubility rate. The granular product is available in 400-pound drums and the crystal product in 50-pound bags.

SAFETY PRECAUTIONS

8

HYDROXYACETIC ACID

Avoid contact with skin, eyes and clothing because this product may cause burns. In case of contact, immediately flush skin or eyes with plenty of water for at least 15 minutes; for eyes, get medical attention.

SULFAMIC ACID

Do not get in eyes because this acid may cause eye injury. Avoid breathing dust and avoid contact with skin and clothing; sulfamic acid may cause irritation of the nose, throat and skin.

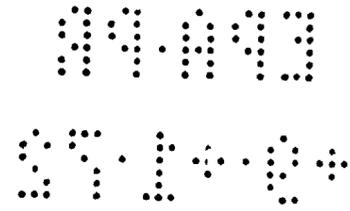
In case of contact, flush skin with water; for eyes, flush with plenty of water for 15 minutes and get medical attention.

When handling either sulfamic acid or hydroxyacetic acid, exposure can be minimized by wearing both goggles and rubber gloves.

REFERENCES

9

1. "What's Your Water-Injection Problem?", Stan Shryock and John Knox, The Oil and Gas Journal, Jan. 4, 1965.
2. "Don't Underestimate Role of Aerobic Bacteria," Gerald A. Trantenberg, The Oil and Gas Journal, Jan. 4, 1965.
3. "The Chemistry of Water Well Development," Frank E. Clarke, Industrial Water Engineering, Sept. 1966.
4. "Iron Bacteria—A New Problem," Grey Culberson, Water Well Journal, Aug. 1963.
5. "Bacteria in Flood Water," J. M. Sharpley, The Petroleum Engineer, Feb. 1961.
6. "New Concepts for Iron Bacteria Control in Water Wells," R. G. Lutby, Water Well Journal, March 1964.
7. "Acidizing the Irrigation Well," Dwayne Konrad, Bulletin FS-290, South Dakota State University, Cooperative Extension Service, United States Department of Agriculture.
8. "Operating and Maintaining Irrigation Wells," Fred Sciner, Bulletin FS-195, South Dakota State University, Cooperative Extension Service, United States Department of Agriculture.



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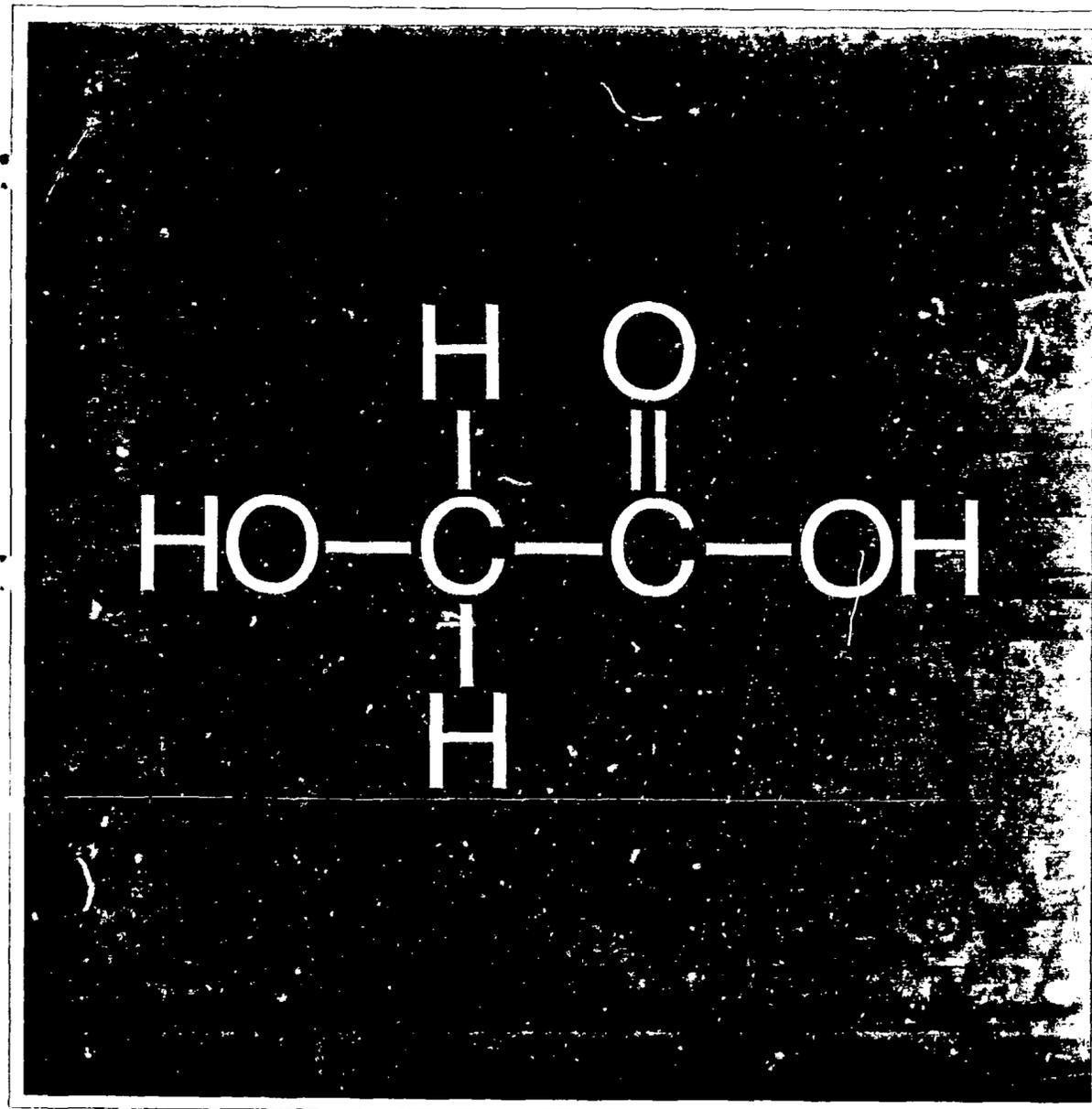
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Better things for better living through chemistry

NEW

HYDROXYACETIC ACID 70% SOLUTION TECHNICAL



DU PONT HYDROXYACETIC ACID 70% SOLUTION TECHNICAL / PRODUCT INFORMATION

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ACCEPTED
Oct. 20, 1972
UNDER THE FEDERAL INSECTICIDE
FUNGICIDE AND RODENTICIDE ACT
FOR ECONOMIC TOXIC SUBSTANCES
LD UNICH NO. 352-304

INTRODUCTION

Hydroxyacetic acid or, as it is sometimes called, glycolic acid, is the first member of the series of alpha hydroxy carboxylic acids. It occurs naturally as the chief acidic constituent of sugar cane juice and also occurs in beet juice and unripe grapes.

The pure acid exists as colorless crystals which are readily soluble in water. Hydroxyacetic acid is non-volatile and cannot be distilled even under reduced pressures. When heated it readily loses water by self esterification to form polyhydroxyacetic acid (polyglycolide).

The acid of commerce is a 70% technical aqueous solution. This solution contains 70% total acid as hydroxyacetic. It contains at least 62.4% free acid. The remaining acidity exists as the polyglycolide which becomes free acid on dilution or neutralization.

Because hydroxyacetic acid is multifunctional and can function as both an acid and alcohol, its reactions are many and its uses are varied. Hydroxyacetic acid finds industrial applications in cleaning, complexing, dyeing, electroplating and as a chemical intermediate.

PROPERTIES

Since aqueous solutions of hydroxyacetic acid contain in addition to the free acid, soluble polyacids, the relative concentration of free acid and polymers is a function of the total concentration of the solution. The equilibrium between free acid and polyacids is established very readily when the solutions are heated. The total acidity of a solution of hydroxyacetic acid even at high concentrations is all ultimately available as free acid because of the ease with which the polyacids are hydrolyzed.

In neutralization reactions, the hydrolysis of the polyacids is greatly accelerated by the presence of alkali. In operations involving the acidification of a solution or adjustment of pH, the final solution is usually so dilute that the polyacids are completely hydrolyzed.

Thus, in nearly all cases it is possible to ignore the fact that part of the hydroxyacetic acid in the 70% solution is present in the form of polyacids, and the solution can be used as if it contained 70% free hydroxyacetic acid. Table I lists the free acid content of various equilibrium solutions of hydroxyacetic acid as well as their melting points.

Bactericidal effects—The bactericidal activity of strong mineral acid is generally agreed to be due to the hydrogen ions present and therefore is measurable by pH. With organic acids however, this is not always true. Reid⁷⁷ has shown that hydroxyacetic acid exhibits bactericidal activity far above that which would be expected due only to the pH of its solutions. Recent studies have shown hydroxyacetic acid to exhibit bactericidal effect on a number of organisms including *Mycobacterium phlei*, *Mycobacterium smegmatis*, *Desulfovibrio desulfuricans*, and *Gallionella ferruginea*.

Solubility—The 70% solution is miscible in all proportions with water and water-soluble organic solvents such as methanol, ethanol, acetic acid, acetone, dioxane, etc. It is immiscible with hydrocarbon, ether, ester, and higher ketone solvents.

See Figures 1, 2 and 3 and Tables I, II and III for additional properties.

Physical Properties

Conductivity (at infinite dilution)	347.9 mhos
Dissociation constant at 25°C	1.5 x 10 ⁻⁴
Heat of combustion	166.6 Kg cal/mol
Heat of solution	11.55 kilojoules/mol
pH at 25°C	0.5
Melting point	10°C (50°F)
Density, 60°F	1.27 g/cc
100°F	1.25 g/cc
140°F	1.24 g/cc
Temperature of the refluxing liquid	112°C (234°F)
Coefficient of thermal expansion (60-140°F)	0.00026/°F
Viscosity at 60°F	11.28 centipoises
Viscosity at 110°F	3.49 centipoises
Pounds per gallon at 60°F	10.6

Average Analysis

Total acid as hydroxyacetic	71.3%
Free acid as hydroxyacetic	64.0%
Formic acid	0.20%
Ash	0.07%
Suspended matter by volume	0.0004%
Color, Gardner	4

TABLE I

Properties of Equilibrium Solutions of Hydroxyacetic Acid

% Total Acid as Hydroxyacetic	% Free Acid as Hydroxyacetic at 25°C	Melting Point, °C
0.0	0.0	0
10.0	10.0	2
20.0	19.9	5
30.0	29.6	9
40.0	39.0	14
50.0	47.7	19
60.0	56.2	25
70.0	64.6	32
80.0	73.0	39
90.0	81.3	47
100.0	88.0	57

⁷⁷All references are listed on page 70.

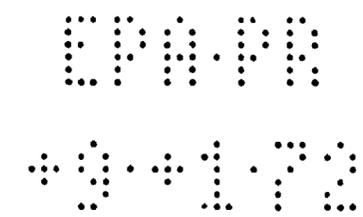
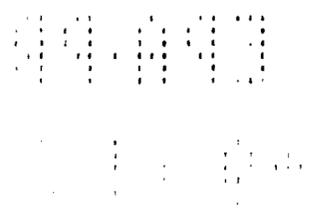


TABLE II HYDROXYACETIC ACID CORROSION DATA

Metal Type	Concentration	Temperature (C)	Inhibitor	Rate (Inches/Yr.)
1020 Steel	5%	71	Rodine 92	0.0364
1020 Steel	5%	71	Rodine 115	0.0497
1020 Steel	10%	66	None	0.1650
1020 Steel	30%	66	None	0.1410
1020 Steel	70%	66	None	0.2170
1021 Steel	2% + 1% formic	93	0.06% Rodine 82A	0.0268
1021 Steel	2% + 1% formic	93	0.06% Rodine 92A	0.1696
1020 Steel	5% + 5% citric + NH ₄ OH to pH 4	100	0.05% Rodine 92	0.339
1020 Steel	5% + 5% citric + NH ₄ OH to pH 4 + 500 ppm Fe	100	0.05% Rodine 92	0.522
1020 Steel	5% + 5% citric + NH ₄ OH to pH 4 + 5000 ppm Fe	100	0.05% Rodine 92	2.15
1020 Steel	(10% Diammonium Citrate)	100	0.05% Rodine 92	0.376
1020 Steel	(10% Diammonium Citrate + 500 ppm Fe)	100	0.05% Rodine 92	0.913
1020 Steel	(10% Diammonium Citrate + 5000 ppm Fe)	100	0.05% Rodine 92	2.72
304 SS	70%	100	None	0.2140
304 SS	70%	100	500 ppm Fe	<0.001
304 SS	5%	71	None	0.00011
304 SS	2% + 1% formic	93	0.06% Rodine 82A	0.0027
304 SS	2% + 1% formic	93	0.06% Rodine 92A	0.0178
304 SS	5% + 5% citric	100	0.05% Rodine 92	0.00015
304 SS	5% + 5% citric + NH ₄ OH to pH 4	100	0.05% Rodine 92	0.00010
304 SS	5% + 5% citric + NH ₄ OH to pH 4 + 500 ppm Fe	100	0.05% Rodine 92	0.00012
316 SS	70%	100	None	0.0800
316 SS	70%	100	500 ppm Fe	<0.001
316 SS	5%	71	None	0.00015
316 SS	2% + 1% formic	93	0.06% Rodine 82A	0.0009
316 SS	2% + 1% formic	93	0.06% Rodine 92A	0.0009
316 SS	5% + 5% citric	100	0.05% Rodine 92	0.00009
316 SS	5% + 5% citric + NH ₄ OH to pH 4	100	0.05% Rodine 92	0.00028
316 SS	5% + 5% citric + NH ₄ OH to pH 4 + 500 ppm Fe	100	0.05% Rodine 92	0.00034
430 SS	70%	100	None	6.240
430 SS	70%	100	500 ppm Fe	0.001
430 SS	10%	100	None	2.9851
430 SS	10%	100	250 ppm Fe	0.011

Metal Type	Concentration	Temperature (C)	Inhibitor	Rate (Inches/Yr.)
446 SS	70%	100	None	5.628
446 SS	70%	100	250 ppm Fe	<0.001
446 SS	10%	100	None	0.6610
446 SS	10%	100	250 ppm Fe	<0.001
Monel	2.3%	30	None	0.0130
Monel	2.3%	100	None	0.0002
Monel	11.3%	30	None	0.0190
Monel	11.3%	100	None	0.0008
Monel	56.4%	30	None	0.0004
Monel	56.4%	100	None	0.0055
Monel	70%	30	None	<0.0001
Monel	70%	100	None	0.0063
Nickel	2.3%	30	None	0.0180
Nickel	2.3%	100	None	0.0025
Nickel	11.3%	30	None	0.0150
Nickel	11.3%	100	None	0.0071
Nickel	56.1%	30	None	0.0003
Nickel	56.1%	100	None	0.0076
Nickel	70%	30	None	0.0002
Nickel	70%	100	None	0.0080
Inconel	2.3%	30	None	0.0040
Inconel	2.3%	100	None	0.0032
Inconel	11.3%	30	None	0.0140
Inconel	11.3%	100	None	0.0046
Inconel	56.1%	30	None	<0.0001
Inconel	56.1%	100	None	0.0110
Inconel	70%	30	None	<0.0001
Inconel	70%	100	None	0.0190
Zircalloy 11	20%	100	0.05% Rodine 92	0.00020
11 (welded)	20%	100	0.05% Rodine 92	0.00011
32	10% + 10% citric	100	0.05% Rodine 92	0.00019
32 (welded)	10% + 10% citric	100	0.05% Rodine 92	0.00021
32	20%	100	0.05% Rodine 92	0.00023
32 (welded)	20%	100	0.05% Rodine 92	0.00018
Zircalloy 11	20%	100	None	0.00019
11 (welded)	20%	100	None	0.00003
32	20%	100	None	0.00033
32 (welded)	20%	100	None	0.00031
Zircalloy 11	10% + 10% citric	100	0.05% Rodine 92	0.00021
11 (welded)	10% + 10% citric	100	0.05% Rodine 92	0.00005
16 Cr, 17 mn, 1 ni	10%	100	None	0.0293
16 Cr, 17 mn, 1 ni	10%	100	250 ppm	0.001
AZ 91, Magnesium	70%	16	None	10.50

FIGURE 1

FREE ACID, VS. TOTAL ACID IN EQUILIBRIUM
SOLUTIONS OF HYDROXYACETIC ACID (TEMP. 25 C)

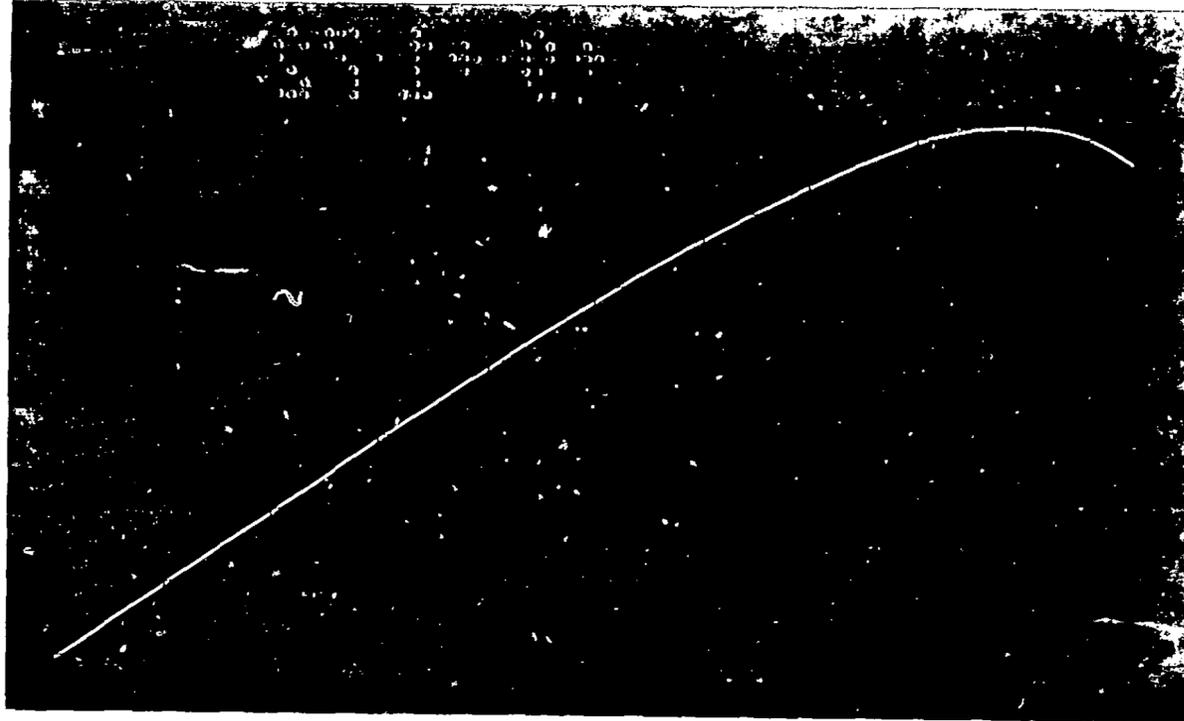


FIGURE 2

MELTING POINTS OF EQUILIBRIUM
SOLUTIONS OF HYDROXYACETIC ACID IN WATER

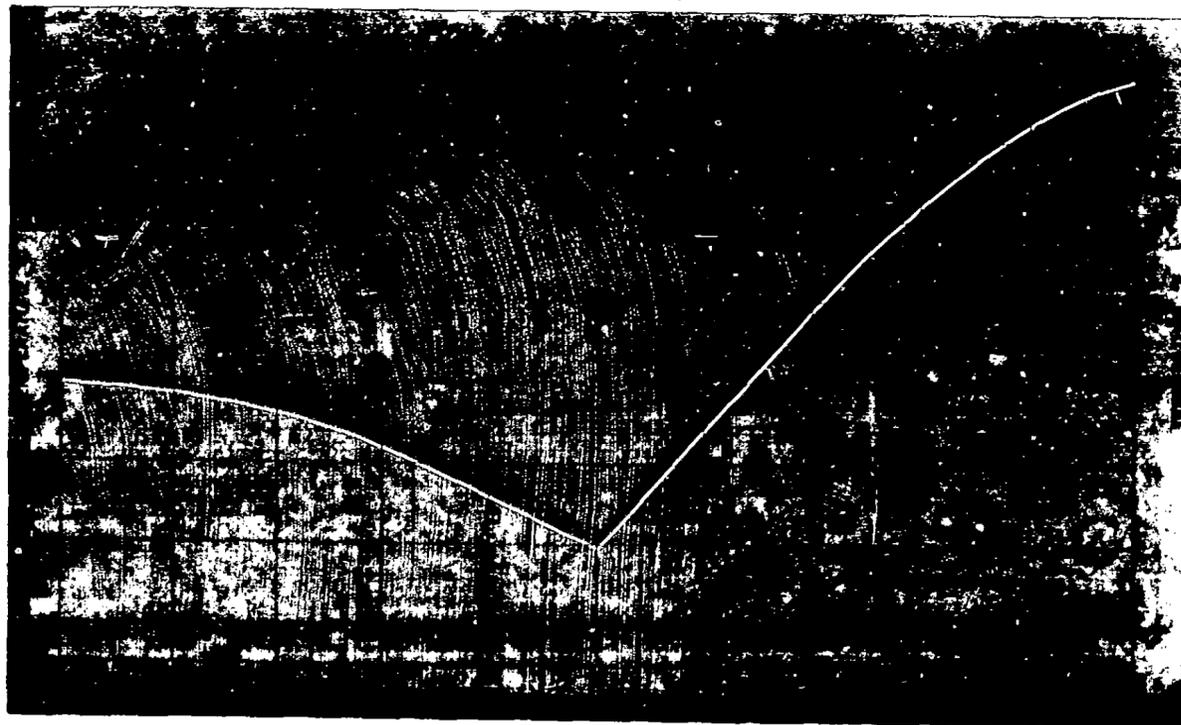
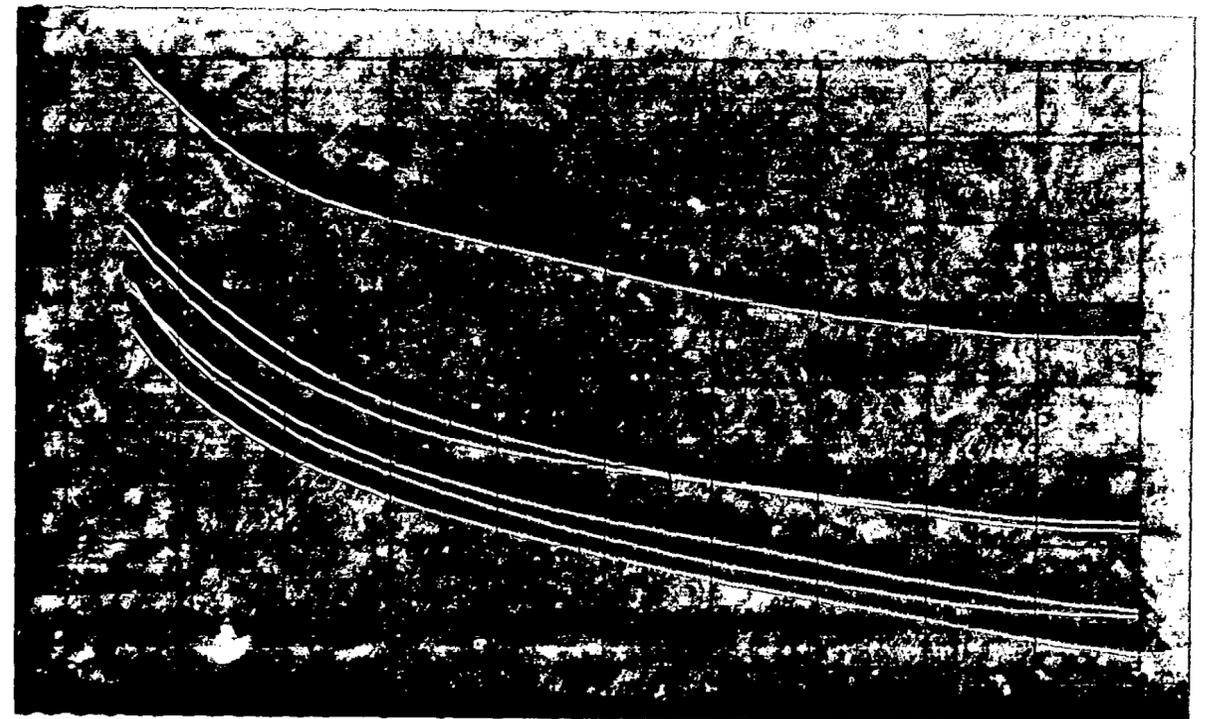


FIGURE 3

pH-CONCENTRATION CURVES (TEMP. 25 C)



0.000
0.001
0.002
0.003
0.004
0.005
0.006
0.007
0.008
0.009
0.010
0.011
0.012
0.013
0.014
0.015
0.016
0.017
0.018
0.019
0.020
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0.022
0.023
0.024
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0.097
0.098
0.099
1.000

FIGURE 2
RELATIONSHIP BETWEEN TOTAL ACID AND FREE ACID

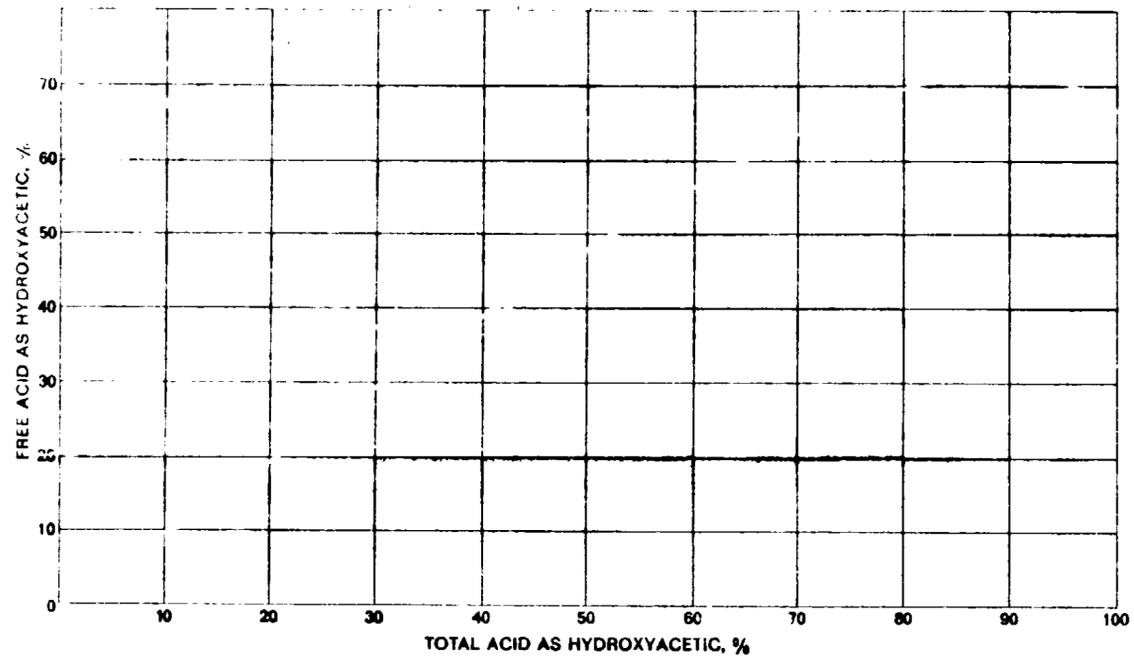


FIGURE 4
RELATIONSHIP BETWEEN TEMPERATURE AND CONCENTRATION OF HYDROXYACETIC ACID IN WATER

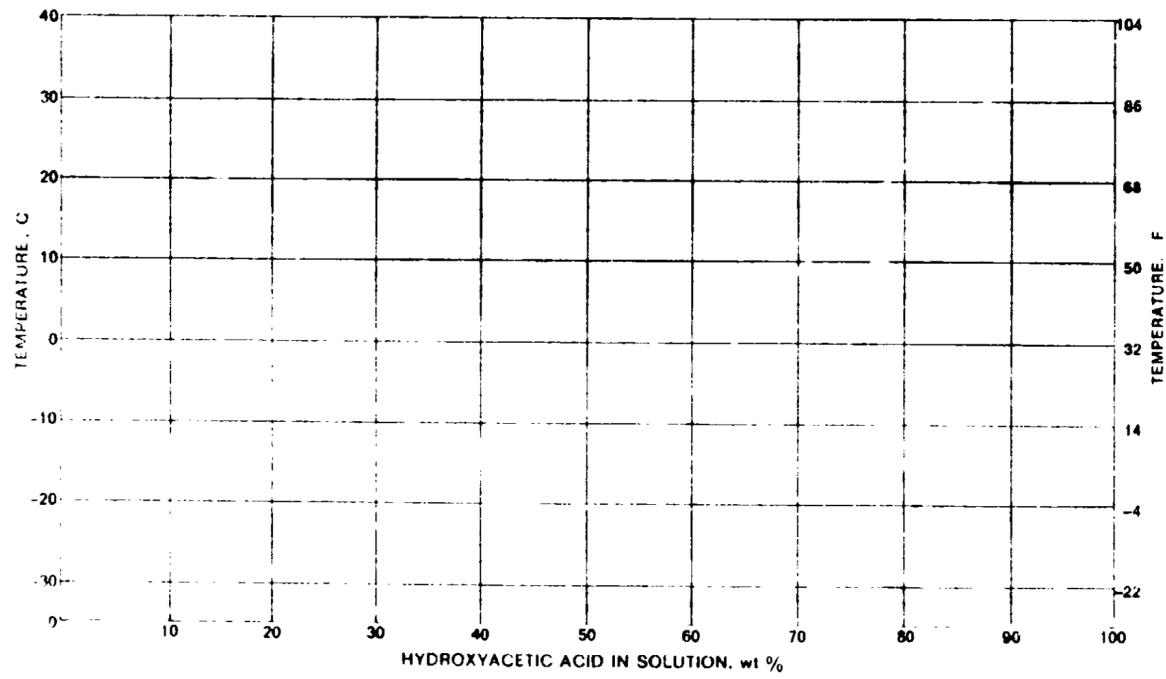
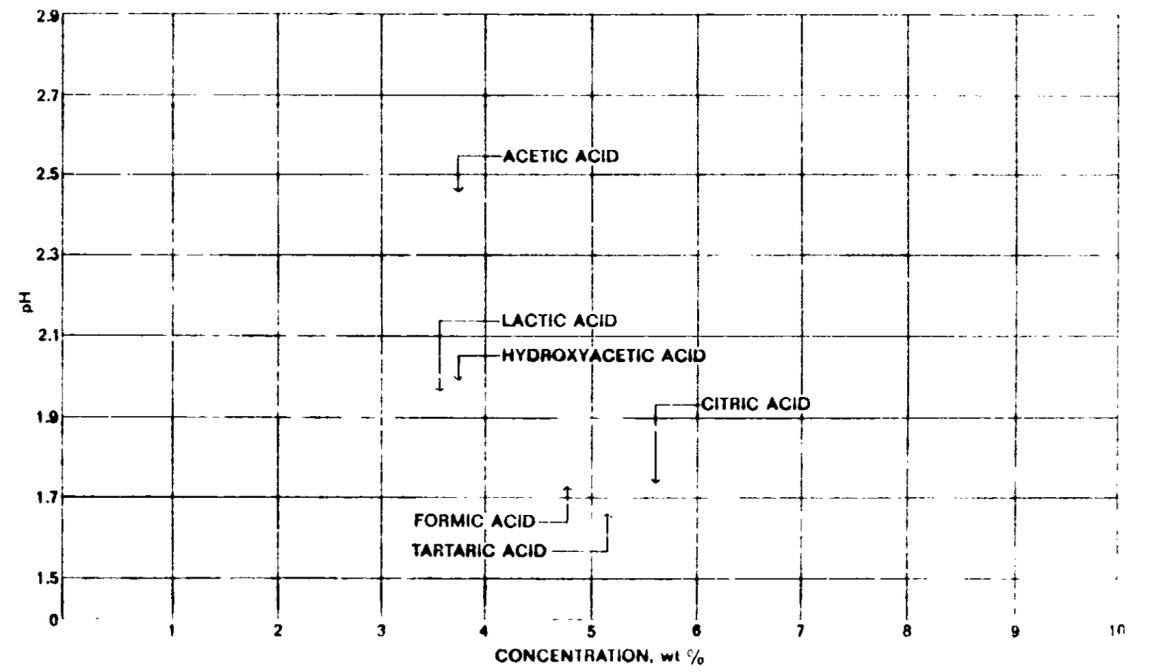


FIGURE 3
pH CONCENTRATION CURVES

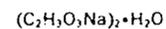
FIGURE 3
pH CONCENTRATION CURVES



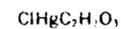
SALTS OF HYDROXYACETIC ACID

A very large number of salts of hydroxyacetic acid have been described in the literature. As a relatively strong organic acid, hydroxyacetic forms stable, slightly hydrolyzed salts, which may be prepared directly by the action of the acid on a metal or metal oxide or hydroxide, or by double decomposition. The alkali and ammonium salts are all hygroscopic and exist as neutral and acid salts, anhydrous and bound with various amounts of water of crystallization.

The following sodium salts are typical:

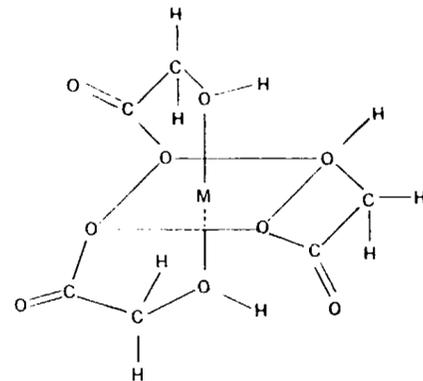


Many double salts have also been reported such as:



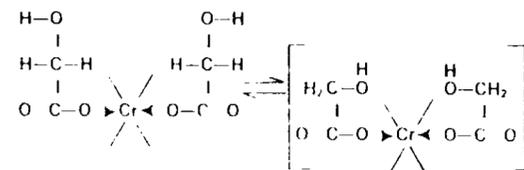
Polyvalent metals form complex hydroxyacetate salts in which both the carboxylic and the alcoholic

hydroxyl groups are involved. General examples of salts of this nature are:



Inner complex salts of bismuth, antimony, and arsenic have been described in the literature in which the trivalent or quinquivalent metal is found in the complex organic anion.¹

Such complexes of chromium have been found to be excellent tanning agents. An illustration of the equilibrium that possibly exists in an aqueous solution is represented by the following structures:⁷⁸



The ability of hydroxyacetic acid to form complexes of this type provides the basis for numerous applications where inexpensive hydroxyacetic acid can substitute for the conventional, more expensive complexing agents. An index of stability constants can be seen in *Stability Constants of Metal-Ion Complexes*, L. G. Sillen and A. E. Martell, The Chemical Society, Burlington House.⁷⁹

A number of metal salts have been studied to determine the degree to which hydroxyacetic acid will delay or eliminate precipitation. Duplicate 0.01 Molar aqueous solutions of the salts were prepared over a range of pH values. The pH range at which precipitation occurred at room temperature was noted. Identical solutions of each salt were observed in the same manner after the addition of enough hydroxyacetic acid (HOAc) to provide four and ten moles of acid for each mole of salt present. Stability constants for most of these complexes have been determined.⁷⁹

When greater complexing strength is required than is afforded by hydroxyacetic acid alone, mixtures of hydroxyacetic acid with other recognized complexing hydroxy acids frequently provide an economical substitute. This is provided by a syner-

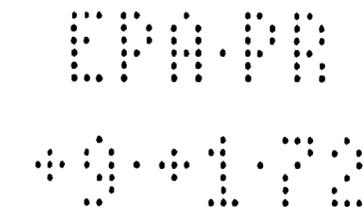


TABLE III
The Complexing Ability of Hydroxyacetic Acid for Selected Metal Ions

Metal Salt ^a Solutions	pH Range in Which the Metal Hydroxides Precipitate			
	10 Moles Acid/Mole of Salt		4 Moles of Acid/Mole of Salt	
	No HOAc	HOAc	No HOAc	HOAc
AgNO ₃	7-8	7-9		
NiCl ₂	8-9	8-9		
CoCl ₂	7-8	8.5-9	7-8	8-8.5
CuCl ₂	5-5.5	7-9	5-5.5	6-7
FeSO ₄	4-6	7-8	4-6	6-7
FeCl ₃	3	10-11	3	4-5
MnSO ₄	5-6	9-11	5-6	5-6
CaCl ₂ ^b	7-8	9-9.5	7-8	7-9
SrCl ₂	10-11	no ppt-Xs NaOH		
Ph(C ₂ H ₃ O ₂) ₂	6-7	6.5-7 ^c		
MgCl ₂	9-10	10-11		
AlCl ₃	6-7	9-10 ^c	6-7	6-7
Al(NO ₃) ₃	6-7	9-10 ^c	6-7	6-7
CrCl ₃	5-7	6-7		

^aNote that the conditions of evaluation in Table III are severe for complexing agents. In practical applications complexing agents are seldom used for metal ion concentrations much higher than 25-50 ppm.

^bIn the case of calcium chloride solution, calcium carbonate precipitates because sodium carbonate has been added.

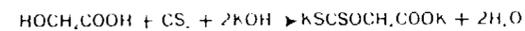
^cThe precipitate redissolves above pH ~ 11.0.

gistic effect between the acids. Such effects have been noted for certain metal ions when mixtures of hydroxyacetic acid and citric or gluconic acids are used.

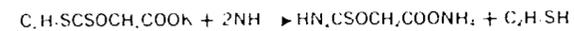
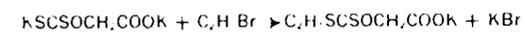
AN. 103

ANHYDRATION

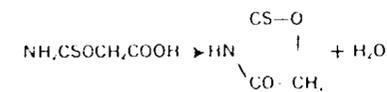
1. Hydroxyacetic acid readily forms the xanthate.



The ethyl xanthate may be formed from this salt after neutralization and the resulting ester treated with ammonia to give the thiocarbamate of hydroxyacetic acid.⁴⁹

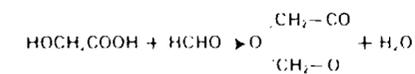


2. Upon heating, thiocarbamyl hydroxyacetic acid is converted into the thiolactam.⁵⁰

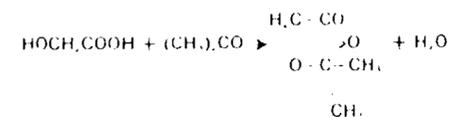


REACTION WITH ALDEHYDES AND RELATED COMPOUNDS

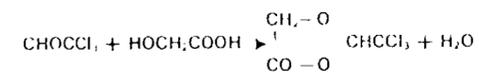
1. With formaldehyde the formal is formed.⁵¹



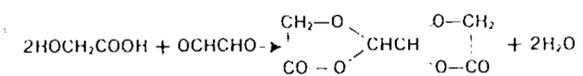
2. With acetone the cyclic ketal is formed.⁵²



3. Chloral reacted with hydroxyacetic gives the chloralide.⁵³

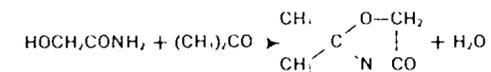


4. With glyoxal the following product is formed.³⁴



These mixed acetals are very reactive and are readily hydrolyzed by water.

5. With hydroxyacetamide, acetone will condense in the presence of HCl to give 2-dimethyl, 4 keto-oxazole.³⁵

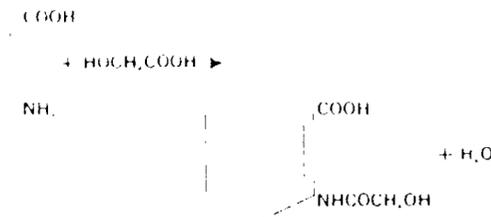


REACTION WITH AMMONIA AND AMINES

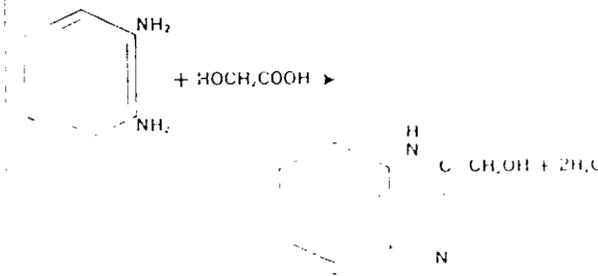
1. Hydroxyacetamide may be readily prepared by the action of ammonia on the polyacid or by treat-

ing an ester of hydroxyacetic with aqueous ammonium hydroxide.

2. Substituted amides are readily prepared by the action of amines on hydroxyacetic acid.⁵⁶



3. The same reaction with o-phenylenediamine will take place followed by a secondary ring closing condensation between the carboxyl and the free amino group.^{57, 58}

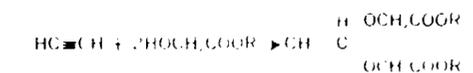


MISCELLANEOUS REACTIONS

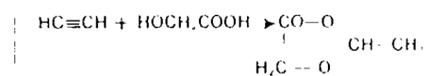
1. Reaction of acetylene with hydroxyacetate esters

EP. 102

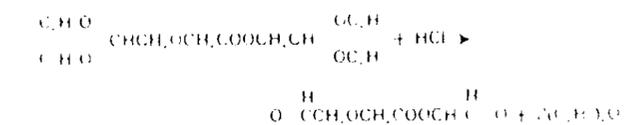
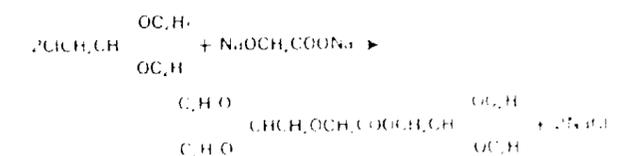
with BF_3 or Hg catalyst gives acetals.⁵⁹



2. Reaction of acetylene with the anhydrous acid using mercury catalyst will provide 2-methyl-4-keto-1,3 dioxane.⁴⁰



3. Dialdehydes can be formed from the basic sodium salt of hydroxyacetic acid and chloroacetal.⁴¹



USES

ESTABLISHED USES

Adhesives—The ability of hydroxyacetic acid to react with casein to form cationic caseinhydroxyacetates finds use in manufacture of certain adhesives and textile sizing compounds.^{45, 47, 48}

Copper Brightening—Hydroxyacetic acid is employed in a bath to give a lustre to copper and copper alloys following the normal pickling operation. This lustre is retained much longer than when strong oxidizing acids are used alone.⁴⁶

Desirable copper utensil polishes are also formulated using hydroxyacetic acid as the main acid ingredient.

Dairy Cleaning—Numerous properties of hydroxyacetic acid contribute to its excellence in functioning as an acid cleaner in removing milkstone deposits from dairy equipment. It dissolves and complexes hard water scale much faster than phosphoric acid. It is superior in its reaction with, and removal of, casein. Hydroxyacetic acid also exhibits definite bactericidal properties, particularly against strains of bovine tuberculosis in or on dairy equipment. It is useful in pH adjustment of iodine sanitizers because of the buffering strength of its salts.^{47, 48}

Decontamination Cleaning—An increasing need exists for efficient means of removing radioactive waste products from reactor loops, power equipment and process equipment. Hydroxyacetic acid fills many of the requirements of these needs.

It is free of metallic ions and is essentially chloride free, thus does not contribute to chloride stress corrosion when used on stainless steel. Hydroxyacetic acid forms complexes with the metals encountered in the residues to be removed. These complexes are soluble but are not as tightly bound as those formed by most recognized complexing agents.

Ammoniated hydroxyacetic acid and mixtures of hydroxyacetic acid and citric acid ammoniated to pH 4.0 show excellent dissolution for the oxides and other salts requiring removal. Hydroxyacetic acid ammoniated to pH 4 gives negligible corrosion to stainless steel, zircalloy and other resistant metals. Ammoniated mixtures of hydroxyacetic acid and citric acid show less corrosion on mild steel than diammonium citrate. The rates are still rather high.

Dyeing—Hydroxyacetic acid has been used extensively in dyeing. It has the advantage of having a mild odor, of being non-volatile and therefore is not lost from dyeing baths at elevated temperatures. It also provides good exhaust and frequently brighter colors. The complexing ability of hydroxyacetic acid is of benefit in complexing metal ions present in the bath water, rinse, etc. Hydroxyacetic acid is most frequently used in wool dyeing. It can be recommended for the dyeing of chrome colors but is not recommended for colors which are easily reduced. Hydroxyacetic acid is a good substitute for cream of tartar in mordanting wool with chrome where it combines good exhaustion with good reduction.^{55, 59}

Electroplating—Numerous applications of hydroxyacetic acid are made in the electroplating industry. The sodium and potassium salts of the acid are excellent substitutes for Rochelle salts used as bath additives.

Inasmuch as hydroxyacetic acid forms complexes with virtually all multivalent metals, its salts form many baths suitable for electroplating.⁷⁹ Excellent plates can be obtained from the chrome, lead, cobalt, tin and nickel salts.

Electroless plating of nickel makes use of hydroxyacetic acid as its sodium salt. The technical 70% product is free of interfering metal ions and sulfur compounds.^{92, 94}

Electropolishing—Electropolishing of stainless steel utilizes hydroxyacetic acid in combination with either phosphoric or sulfuric acids. The mixture provides a bath with long life and excellent sludging characteristics.

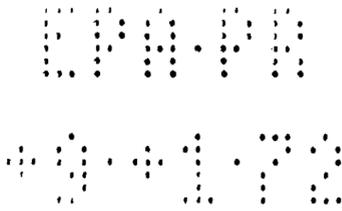
Etching—Hydroxyacetic acid is utilized in the etching of lithograph plates. It is also useful in prevention of unwanted precipitates by forming many soluble metallic complexes in both alkaline and acid environments. It has value in chemical milling and many cleaning formulations.⁷

Masonry Cleaning—Mixtures of hydroxyacetic acid and phosphoric acid are finding use as a masonry cleaner, both in the manufacture of bricks and in the cleaning of freshly laid brick and tile. Certain clays used in making white bricks contain traces of metals which migrate to the surface during firing causing staining. Hydroxyacetic acid is particularly effective in removing these stains due to its complexing ability for metals.

Metal Pickling—Hydroxyacetic acid has replaced volatile organic acids in certain pickling operations. The nonvolatile characteristic prevents losses due to elevated temperatures and reduces the ventilation requirements. In general it can usually be used to replace any organic acid in pickling formulations.

Paper Felt Cleaning—Because of aluminum complexing strength as well as hard water salt dissolution ability, hydroxyacetic acid should be valuable in conditioning paper felts. It is non-injurious to the wool and nylon used in construction of paper felts.

Petroleum Emulsion Breaking—Numerous derivatives of hydroxyacetic acid esters are utilized in resolving oil-water emulsions. Numerous patents have been issued covering the production of these derivatives.^{7, 10}



Petroleum Lubricating Oil—Modified lubricants containing additives formulated from hydroxyacetic acid and polyhydric alcohols impart desirable extreme pressure lubrication properties.^{10, 11} Hydroxyacetic acid has also been used to remove metallic impurities from fats and oils by extraction with an aqueous solution of the acid to form soluble metallic complexes which are then removed by decantation.^{7, 10}

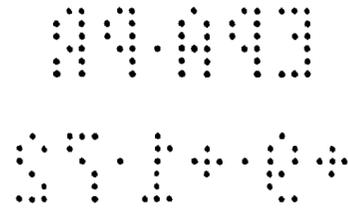
Stainless Steel Boiler and Process Equipment Cleaning—The absence of chloride ion gives assurance of freedom from damage due to chloride stress corrosion. Calcium carbonate, mill scale and magnetic iron oxide all can be removed at no sacrifice in speed or cost by hydroxyacetic acid or mixture of hydroxyacetic and formic acid. The mixture (two percent hydroxyacetic acid, one percent formic acid) has been developed particularly for cleaning high pressure stainless steel steam generators.⁷ This mixture offers the following advantages: (1) effective removal of operational and preoperational deposits, (2) freedom from organic iron precipitation, (3) no chlorides, (4) low corrosion, (5) economy and (6) volatile decomposition products.

The iron salts resulting from these mixed acids exhibit higher solubility and less tendency to precipitate than when either of these acids are used singly. This permits longer contact time and more deposit removal with lessened danger of plugging due to precipitation.

The thermal decomposition products of hydroxyacetic acid at 400°C and 4500 psi are carbon monoxide, formaldehyde, and a trace of formic acid, all of which are volatile.

Corrosion rates of hydroxyacetic acid on stainless steel are very low.

Tanning—In the tanning process, hydroxyacetic acid is frequently used to replace mineral acids



where high quality leather is desired. It is used in the delimiting operation, adjustment of pH during tanning and during dyeing.

During the tanning operation, hydroxyacetic acid serves a dual purpose. It is used to adjust the pH of the vegetable tanning liquor and to prevent staining of the leather caused by the formation of highly colored metal tannin salts. Salts of the acid are used as masking agents. A new compound obtained by reaction of sodium dichromate with hydroxyacetic acid tris-hydroxyacetato chromiate is an effective and rapid tanning agent. Similar compounds are formed with zirconium and titanium salts which give white tannages. Tanning agents are also formed by hydroxyacetic acid condensations with products like tetrahydronaphthalene.^{72, 76}

Water Well Cleaning—Much of what has already been said concerning oil well cleaning applies to water well cleaning, too. Hydroxyacetic acid complexes and removes light iron and carbonate scales while preventing reprecipitation when the acidity is dissipated. Unlike the mineral acids, hydroxyacetic is very mildly corrosive to metals and will not damage well metals.

Hydroxyacetic acid controls the *Gallionella* iron bacteria, which causes precipitation of iron oxide, and inhibits regrowth of these bacteria. The use of hydroxyacetic acid in well cleaning minimizes the need for separate addition of complexing agents and bactericides. It can function efficiently to replace these different agents because treatment with hydroxyacetic acid performs all three functions of cleaning, complexing iron, and bacterial control. Hydroxyacetic acid, however, does not replace the need for phosphate treatment used to aid clay removal. It may also be used in admixture with other acids, such as sulfamic acid.

FOOTNOTES

Oil Well Acidification and Secondary Recovery—Hydroxyacetic acid exhibits complexing ability for

iron at much below the cost of conventional chelating agents. In conjunction with hydrochloric acid or sulfamic acid it prevents iron precipitation in cleaning operations or in water flooding. Definite bactericidal properties exist with this acid in addition to that attributed to pH alone, reducing problems of metal deposition and corrosion due to bacterial action. Hydroxyacetic acid costs less than other organic acids used in this type of treatment.

Vapor Cleaning—Vapor cleaning is a technique for cleaning pipe lines by injection of acid solutions into a steam jet blowing steam through the pipe. Mill scale is removed by the dual function of the acid attack coupled with the turbulence and velocity associated with the stream flow. The corrosion rates encountered when using hydroxyacetic acid are comparable to those of the other accepted acids used in this type of cleaning. The speed of cleaning or removing the mill scale is such that contact times are at a minimum and corrosion of the base metal is at a minimum. Hydroxyacetic acid 70% technical commercial solution requires only dilution to prepare it for this type of cleaning and it serves as an economical substitute for other acids now used conventionally with no sacrifice in performance.

Metal Cleaners—Hydroxyacetic acid, exhibiting complexing power and oxide solubility for many metals, makes it a candidate for inclusion in metal cleaning formulations. It will be of value in airplane, train and truck body cleaning. It also should be considered for missile component cleaning. Hydroxyacetic acid is presently used in missile fuel compartment cleaning.

Hard Water Scale—Hydroxyacetic will effectively remove hard water scale from all types of heat exchange equipment. It should be considered for pH adjustment of cooling waters to prevent scale buildup.



Hydroxyacetic acid is corrosive to iron, mild steel, chrome steel, tin and aluminum. Lead is initially attacked but forms a resistant film. Copper and bronze are resistant in the absence of air. Stainless steel and silver (fine and sterling) are resistant over a wide range of temperature and acid concentrations.

Storage tanks constructed of 304 stainless steel are recommended for storage at temperatures up to 160°F, and 316 stainless steel for temperatures above 160°F. "Heresite" lined mild steel or wooden storage tanks can also be used at ambient temperatures.

Because of the 10°C freezing point of hydroxyacetic acid, bulk storage tanks in unheated locations should be equipped with heating coils for thawing in winter temperatures and pump lines arranged to allow recycling through the tank for mixing. Drums should be stored in heated warehouses.

Piping can consist of 304 or 316 type stainless steel as well as neoprene. Piping in areas exposed

to low temperatures should be steam traced or electrically heated.

A centrifugal pump is quite suitable for unloading into storage and transfers. Pumps similar to Type SSO (Allis Chalmers, Norwood, Ohio), are recommended for use with hydroxyacetic acid.

HANDLING PRECAUTIONS

Hydroxyacetic acid is a fairly strong organic acid and the concentrated 70% solution may cause burns. Contact of the acid with skin, eyes and clothing should be avoided. Exposure can be minimized by wearing chemical goggles and rubber gloves when handling hydroxyacetic acid solutions. Additional protective clothing, such as rubber pants, and jacket, rubber safety shoes and rubber gauntlets may be desirable where probability of contact with hydroxyacetic acid solutions is high.

In case of contact, immediately flush skin or eyes with plenty of water for at least 15 minutes; for eyes, get medical attention.

TOXICOLOGY

ORAL

Using the classifications set forth by Hodge and Sterner, American Industrial Hygiene Association Quarterly 10:4, 93, December 1943, hydroxyacetic acid is moderately toxic when ingested. The lethal oral dose of hydroxyacetic acid, as the sodium salt, for cats is approximately 500 mg per kg of body weight.¹ Its toxicity may be somewhat less for man, since Milhorat and Toscani² reported no toxic symptoms in patients with muscular dystrophy who received oral doses of 260 to 400 mg per kg of

sodium hydroxyacetate daily for periods up to 7 days.

SKIN

No specific skin absorption toxicity or local irritation studies have been reported, but since hydroxyacetic acid is a fairly strong organic acid, avoid contact with skin, eyes, and clothing.

INHALATION

Hydroxyacetic acid is nonvolatile, but breathing of spray or mist should be avoided.

PACKAGING

3,000- to 4,000-gallon tank trucks and 6,000-, 7,000-, and 10,000-gallon tank cars (approximately 30,000- to 40,000-, 60,000-, 70,000-, and 100,000-lb 70% solution, respectively). Tank

cars have special acid resistant lining, are insulated and have exterior heating coils. Also supplied in PE fiber drums, average net weight 550 lb.

FIGURE 4 CALCIUM CARBONATE DISSOLUTION RATES

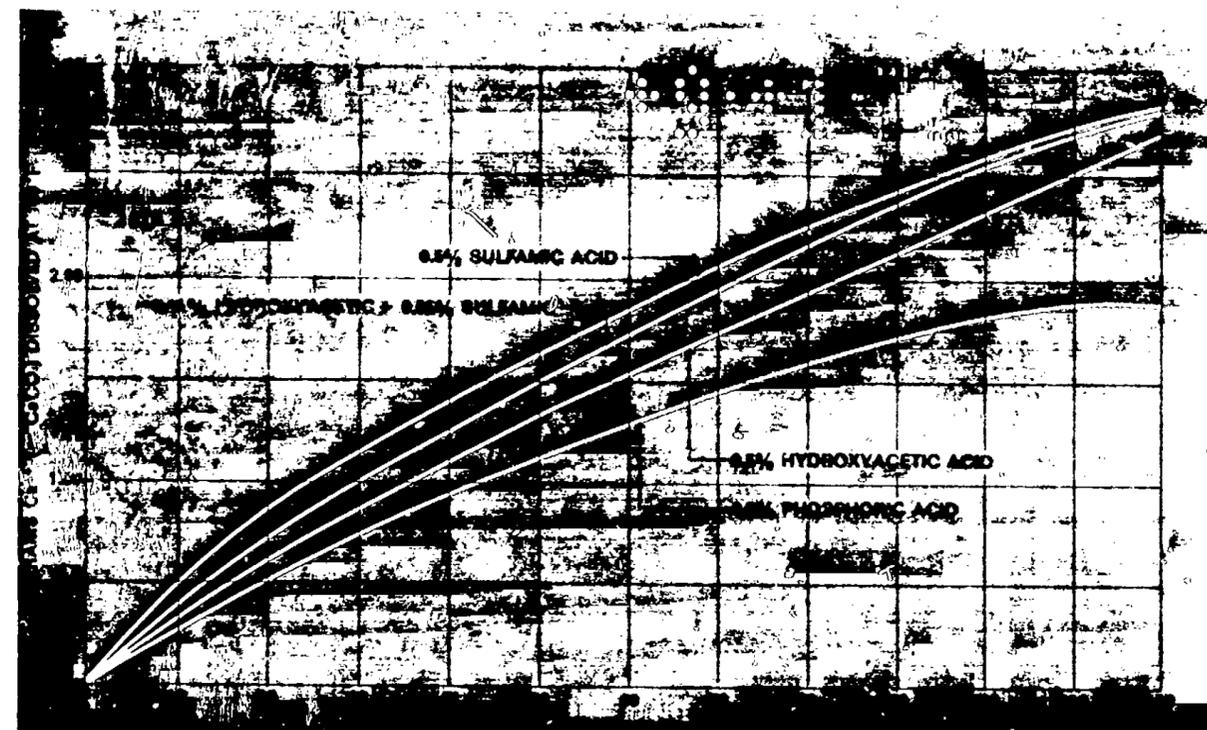
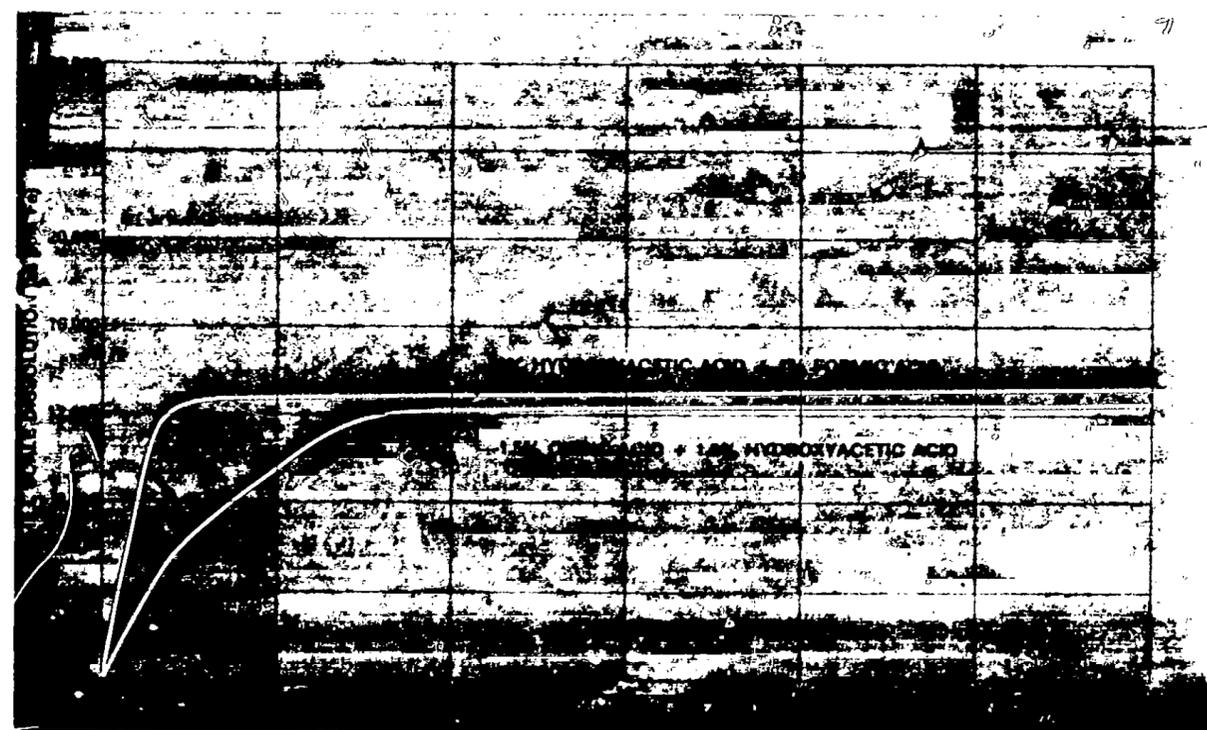


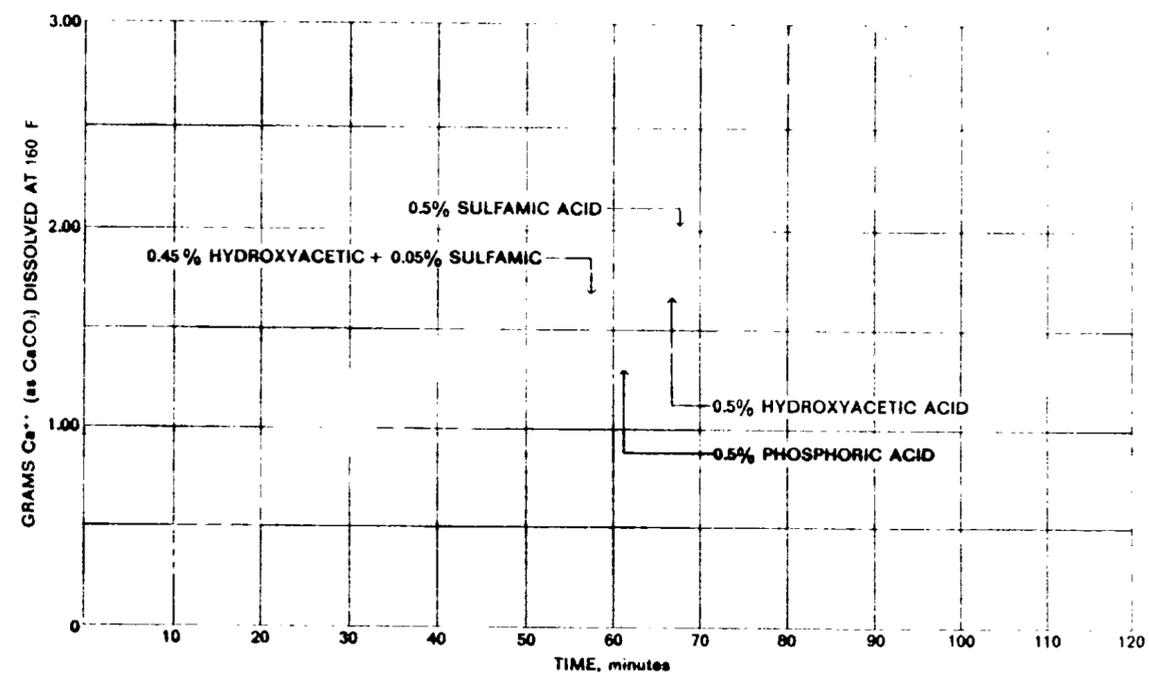
FIGURE 5 MILL SCALE DISSOLUTION BY HYDROXYACETIC-FORMIC MIXTURES AT 100 C



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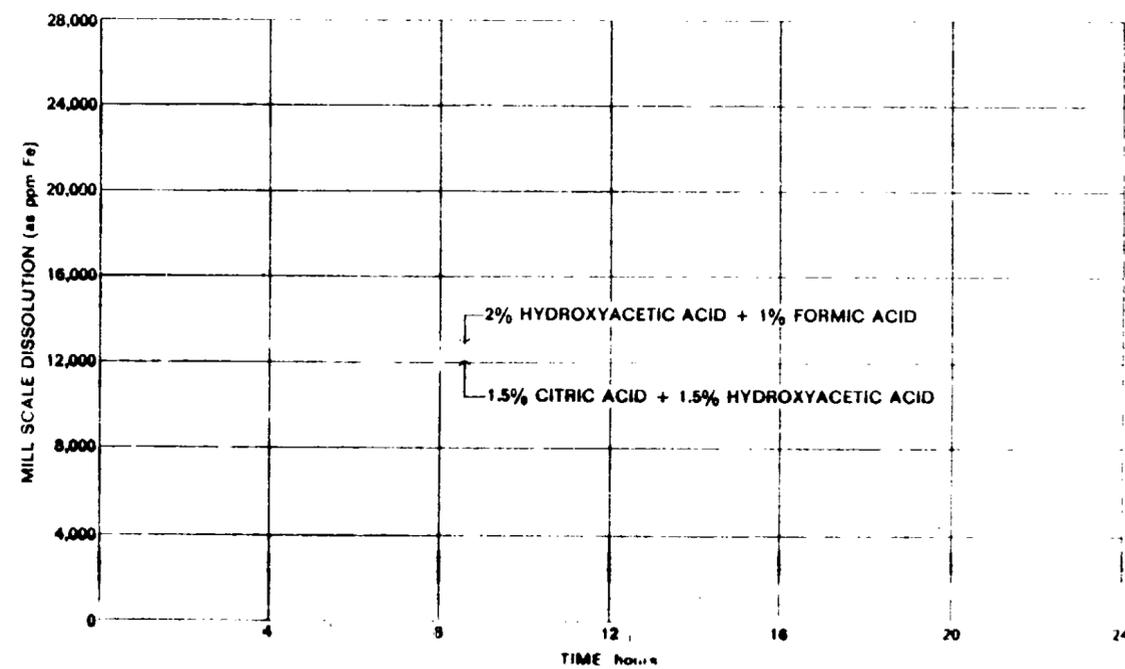
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FIGURE 4 MILL SCALE DISSOLUTION BY HYDROXYACETIC ACID



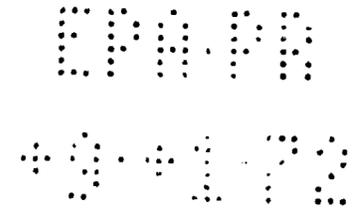
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FIGURE 5 MILL SCALE DISSOLUTION BY HYDROXYACETIC-FORMIC MIXTURE AT 160 F



REFERENCES

1. Rosenheim, et al., *Z. Anorg. Allgem. Chem.* 200, 173 (1931).
2. A. Claus, *Ann.* 145, 256 (1868).
3. H. J. H. Fenton & H. O. Jones, *J. Chem. Soc.* 77, 70 (1900).
4. S. Goldschmidt, P. Askenary & S. Pierros, *Ber.* 61B, 223 (1928).
5. H. Wieland and W. Franke, *Ann.* 457, 170 (1927).
6. H. Wieland and H. Lovenskiold, *Ann.* 436, 229-262 (1924).
7. W. S. Denham and H. Woodhouse, *J. Chem. Soc.* 103 (1861).
8. Heintz, *Ann. d. Physik.* 115, 461 (1861).
9. E. Drechsel, *Ann.* 127, 159 (1863).
10. Fittig and Thompson, *Ann.* 200, 79 (1880).
11. E. J. Witzemann, *J. Am. Chem. Soc.* 39, 111 (1917).
12. C. A. Bischoff and Walden, *Ber.* 26, 262 (1893).
13. R. Anschutz and Bertram, *Ber.* 36, 466 (1902).
14. U.S. Patent 1,927,295 to E. J. Powers, 9-19-33.
15. U.S. Patent 1,947,463 to H. Dreyfus, 1934.
16. U.S. Patent 1,972,134 to H. Dreyfus, 1934.
17. German Patent 480,866 to Consortium fur Elektrochemische.
18. H. Duval, *Bull. Soc. Chim.* (3) 29, 601-678 (1903).
19. Henry, *Ann. de Chim.* (4), 28, 424.
20. French Patent 684,814 to H. Kaufmann, 1930.
21. A. Kekule, *Chem. Centralblatt* 35, 665 (1864).
22. U.S. Patent 2,876,255 (1959).
23. British Patent 650,003, *J. C. S.* 1950, 1357-1359.
24. W. Heintz, *Ann.* 154, 257-69 (1870).
25. Thiel and Dent, *Ann.* 302, 245-272 (1898).
26. Emil Fischer and H. O. L. Fischer, *Ber.* 47, 768 (1914).
27. E. Clemmensen and A. H. C. Heitman, *Am. Chem. J.* 42, 319-340.
28. E. Lambing, *Comp. Rend* 127, 64-67 (1897), 127, 188-190 (1897).
29. B. Holmberg, *J. Pr. Chem.* 75, 169-87, *Ibid.* 71, 291.
30. O. Wallach, *Ann.* 193, 35 (1878).
31. C. A. Lohry de Bruyn and Alberda von E., *Rec. Trav. Chim.* 20, 331 (1901), 21, 310-20 (1902).
32. K. Willstaetter & F. Koenigsberger, *Ber.* 56, 2107 (1923).
33. O. Wallach, *Ann.* 193, 35 (1878).
34. H. O. L. Fischer & C. Traube, *Ber.* 59, 851-56 (1926).
35. H. O. L. Fischer, Dauschat, and Stettiner, *Ber.* 65, 1032-1037 (1932).
36. German Patent 153,576 (1904).
37. A. Bistrzycki & G. Przeworski, *Ber.* 45, 3483-95 (1912).
38. M. A. Phillips, *J. Chem. Soc.* (1928), 2313-99.
39. U.S. Patent 2,387,495.
40. British Patent 573,087 (1945).
41. F. Groth, *Swensk Kem. Tidn.* 69, 245-6 (1948), *CA* 7577, 43 (1949).
42. Steven Krop and Harry Gold, *J. Am. Pharm. Assoc.* 34, 86-9 (1945).
43. W. F. Riker and Harry Gold, *J. Am. Pharm. Assoc.* 31, 306-312 (1942).
44. Milhorat, A. T., and Toscani, V., *J. Biol. Chem.* 114 (1936), 461.
45. U.S. Patent 2,757,097.
46. U.S. Patent 2,382,865 (1942).
47. U.S. Patent 2,320,087 (1941).
48. U.S. Patent 2,342,739 (1941).
49. U.S. Patent 2,338,688 (1944).
50. U.S. Patent 2,338,689 (1944).
51. J. D. Reid, *Am. J. Hygiene* 16, 540 (1932).
52. M. H. Fischer and W. J. Suer, *Arch. Path.* 17, 615-19 (1934).
53. N. Isgaryschew and A. Pomeranzeva, *Kolloid-Z* 38, 235.
54. F. Takelenburg, *C. A.* 22, 2385 (1928).
55. U.S. Patent 1,059,740 (1913).
56. British patent 183,813 (1922).
57. British patent 205,166 (1923).
58. British patent 277,414 (1927).
59. German patent 256,858 (1913).
60. German patent 260,897 (1913).
61. U.S. Patent 2,532,283.
62. U.S. Patent 2,532,284.
63. A. Brenner and Grace Riddell, *J. Research NBS* 37, 31 (1946).
64. *Proc. Am. Electroplaters Soc.* 33 (1946).
65. U.S. Patent 2,270,712, W. H. Wood to Harris-Seybold-Potter Co. (1940).
66. U.S. Patent 2,322,494, A. F. Wirtel and C. M. Blair to Petrolite Corp.
67. U.S. Patent 2,340,355, A. F. Wirtel to Petrolite Corp.
68. British patent 792,186 (1958), N.V. DeBataafsche Petroleum.
69. U.S. Patent 2,311,653, B. B. Farrington, R. K. Humphries, and R. T. Macdonald to Standard Oil of California.
70. German patent 309,157 to Elektro-Osmose Akt. Ges.
71. German patent 309,275 to Elektro-Osmose Akt. Ges.
72. German patent 309,276 to Elektro-Osmose Akt. Ges.
73. British patent 171,956 to Elektrochemische Werke Ges.
74. German patent 380,593 to Elektrochemische Werke Ges.
75. German patent 386,930 to Elektrochemische Werke Ges.
76. German patent 433,163 to I.G. Farbenindustrie Akt. Ges.
77. Reid, J. D., *Amer. J. Hyg.* 15, 540-556 (1932).
78. Ramaswamy, D. Y. Nayudamma, *J. Am. Leather Chemists Ass'n.* 52, 67 (1957).
79. Sillen, L. G. and A. E. Martell, *Stability Constants of Metal Ion Complexes*, Special Publication 17, London: The Chemical Society, Burlington House, 1964.
80. McLaughlin, L. G., *Materials Protection*, Vol. 2, No. 8, pp. 52, 54, 57 (1963).



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