CRUDE OIL SWEETENING WITH A NOVEL AND SELECTIVE ALKANOLAMINE

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INTRODUCTION

Hydrogen sulfide gas is present in much of the crude oil and natural gas production throughout the world. This creates quite a problem for today's producers, in that the hydrogen sulfide is both poisonous and very corrosive. In the past, the need to reduce hydrogen sulfide (H_2S) by "sweetening" was born more of necessity than environmental good intentions. The high toxicity of H_2S simply made it imperative. It is only in recent years that scientists have discovered that these gases also contribute to acid rain and the destruction of our irreplaceable ozone layer.

Now, with the addition of these serious environmental implications, the issue of sweetening produced oil, gas, and water containing H_2S has taken on an even greater importance. Unfortunately, addressing this environmental responsibility is further complicated by old gas sweetening techniques that have traditionally forced you to accept certain compromises in efficiency, cost of production, and even the quality of your end product. Many of these methods of H_2S removal involve the use of heavy metals and known carcinogens that result in a waste product which is hazardous to man and the environment, as well as having the requirement of being disposed of at an EPA approved disposal site. In addition, these methods are known to be non-selective in their removal of H_2S, also combining with large quantities of carbon dioxide, compromising the quality of your finished product. Essentially, wasting product by removing carbon dioxide from your production rather than simply getting the H_2S out.

CHEMISTRY

A new patented alkanolamine product has been developed that selectively reacts with hydrogen sulfide in produced gas, oil, and water that may contain any amount of carbon dioxide. The method is comprised of, in part, the use of products known as triazines. A representative of this class of compounds is the 1,3,5 tri-(2 hydroxyethyl)-hexahydro-S-triazine. On a molar basis, one mole of this triazine will react with four moles of H_2S to form dithiazine and bis-dithiazine products. These reaction products are completely water soluble and have been classed by the EPA as non-hazardous.

FEATURES AND CHARACTERISTICS

The following list highlights some of the features and characteristics of a triazine:

- The triazine product is a liquid.
- The reaction between the triazine and the H_2S is virtually instantaneous.
- The triazine product reacts selectively with H_2S. It does not react with CO_2.

- The reaction product is a liquid. No solids are formed.

- The reaction product is an excellent water soluble corrosion inhibitor and may be used in a variety of ways. Corrosion data is presented in Table I(A), I(B), II(A), and II(B).

- When viewed as a waste material, the liquid reaction product is non-hazardous and low in toxicity. A hazardous waste analysis of a typical sample of reaction product is found in Table III. Toxicity studies are summarized in Table IV.

TRIAZINE PRODUCT - APPLICATION TECHNOLOGY

In order to successfully apply the example triazine product, it is necessary to provide a place or places in a system that will permit intimate contact between the triazine and H_2S. The following four factors are responsible for the product management versatility associated with the triazine technology:

1. The triazine product is a liquid.

2. The triazine reacts selectively with H_2S to form stable reaction products.

3. The triazine/H_2S reaction products are water soluble.

4. The triazine/H_2S reaction products are excellent corrosion inhibitors.

This triazine product is currently being applied to crude oil produced from wells in the Plaza and Wabek fields in Mountrail County, North Dakota. The H_2S concentration in these wells varies from a high of 1,195 ppm to a low of 507 ppm. With an average concentration of 850 ppm, the necessary quantities of triazine are being added to remove 500 ppm from the crude oil stream. The triazine product is being applied through a specially designed quill that introduces the product into the middle of the pipeline containing the crude oil. This injection point is immediately upstream of the specially designed static mixing system, thus providing intimate contact of the triazine with the H_2S in solution in the produced crude. Mixing of this product is a very critical point in the successful application and removal of H_2S, thus the engineering calculations must be done with precision and careful attention to detail. The net result of this project is that over 200,000 barrels of produced crude oil have been sweetened to pipeline specifications and thus a premium price has been realized by the producer. In addition, the lower H_2S levels in the produced crude oil open up new markets for possible sale of the produced oil.

CONCLUSIONS

The triazine product may be used in a variety of ways, often with existing or slightly modified equipment. The absence of produced solids allows for continuous operations, thereby eliminating expensive downtime. The H_2S reaction product is non-hazardous and is an excellent water soluble corrosion inhibitor.

Although there are no chemical limits with respect to the maximum amount of H_2S that may be removed from gas or hydrocarbon liquids by the triazine product, economic and/or environmental considerations will dictate its selection.

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Table I (A)
Wheel Test Data

Spent Triazine Product Removed from a Contact Tower - Polk County, Texas
Sample Date: August 2, 1990

TEST CONDITIONS:
Type Test - Continuous Treatment
Acid Gas - Saturated Carbon Dioxide
Test Temperature - 150° F
Liquid Volume - 180 ml
Liquid Composition -
90% NACE Recommended Brine
10% Depolarized Kerosene
Exposure Time - 24 Hours
Type Coupon - Sandblasted Mild Steel Shimstock

PROCEDURE:
Each Test Cell was charged with 180 ml of test liquid and a weighed coupon was inserted. Each cell was then sparged with CO_2 to saturation.

TEST RESULTS:

ppm Spent Triazine Product	% Protection
12.5	70.3
25.0	77.0
37.5	81.8
50.0	82.5
75.0	85.2
200.0	92.0

Table I (B)
Wheel Test Data

Spent Triazine Product Removed from a Contact Tower - Polk County, Texas
Sample Date: August 2, 1990

TEST CONDITIONS:
Type Test - Continuous Treatment
Acid Gas - Saturated Carbon Dioxide
+ 500 ppm H_2S
Test Temperature - 150° F
Liquid Volume - 180 ml
Liquid Composition -
90% NACE Recommended Brine
10% Depolarized Kerosene
Exposure Time - 24 Hours
Type Coupon - Sandblasted Mild Steel Shimstock

PROCEDURE:
Each Test Cell was charged with 180 ml of test liquid and a weighed coupon was inserted. The cell was then saturated with CO_2, after which 500 ppm H_2S was added.

TEST RESULTS:

ppm Spent Triazine Product	% Protection
12.5	17.8
25.0	37.0
37.5	57.8
50.0	69.9
75.0	78.9
200.0	81.6

Table II (A)
Wheel Test Data

Spent Triazine Product Removed from a Contact Tower - Limestone County, Texas
Sample Date: September 14, 1990

TEST CONDITIONS:
Type Test - Partioning, Continuous Treatment
Acid Gas - Carbon Dioxide
Test Temperature - 150° F
Exposure Time - 24 Hours
Type Coupon - Sandblasted Mild Steel Shimstock

PROCEDURE:
An 80% depolarized kerosene/20% NACE recommended brine mixture was purged overnight with CO_2. The mixture was charged with 50 ppm spent Triazine product and was mixed by shaking the sample 50 times. After standing for one hour, the aqueous layer was drained into a test cell containing a weighed coupon. The cell was rotated on a wheel for 24 hours at 150° F. An untreated sample provided the blank.
The blank lost 55.8 mg and the protected coupon lost 2.5 mg.

$$\text{The \% protection is } \frac{55.8 - 2.5}{55.8} \times 100 = 95.5\%$$

Table II (B)
Wheel Test Data

Spent Triazine Product Removed from a Contact Tower - Limestone County, Texas
Sample Date: September 14, 1990

TEST CONDITIONS:
Type Test - Continuous
Acid Gas - Saturated CO_2 + 100 ppm H_2S
Test Temperature - 150° F
Liquid Volume - 180 ml
Liquid Composition -
100% NACE Recommended Brine
Exposure Time - 24 Hours
Type Coupon - Sandblasted Mild Steel Shimstock

PROCEDURE:
Each test cell was charged with 180 ml of test liquid and weighed coupon was inserted. Each cell was then sparged with CO_2 to saturation followed by the addition of 100 ppm H_2S

TEST RESULTS:

ppm Spent Triazine Product	% Protection
25	70.5
50	80.5
75	85.0
100	87.9
150	91.6

Table III
Hazardous Waste Analysis of Typical Spent Triazine Product

PARAMETER	RESULTS	LIMIT
Ignitability		
Flash Point °F	>212	140 Minimum
Corrosivity		
pH	7.08	>2 or <12.5 Maximum
Corrosion rate	Non-corrosive	0.25 in./yr. Maximum
Reactivity		Maximum Allowable
Sulfide	Non-reactive	500 ppm
Cyanide	Non-reactive	250 ppm

	CONCENTRATION, PPM	
EP Toxicity	Actual	Max. Allowable
Arsenic	ND	5.0
Barium	4.5	100.0
Cadmium	ND	1.0
Chromium	ND	5.0
Lead	ND	5.0
Mercury	ND	0.2
Selenium	ND	1.0
Silver	ND	5.0
Lindane	ND	0.4
Endrin	ND	0.02
Methoxychlor	ND	10.0
Toxaphene	ND	0.5
2,4-Dichlorophenoxyacetic Acid	ND	10.0
2,4,5-Trichlorophenoxypropionic Acid	ND	1.0

ND = Not Detected

Table IV
Toxicity Studies - Reacted Triazine Product

Single Dose Oral Toxicity in Rates

Test Results: The LD 50 is greater than 5.0 g/kg of body weight.

Primary Dermal Irritation in Albino Rabbits

Test Results: Reacted Triazine product is a non-irritant.

Primary Eye Irritation/Corrosion in Rabbits

* Eye irritation is the production of reversible changes in the eye following application of the test article to the anterior surface of the eye.

* Eye corrosion is the production of irreversible tissue damage to the eye following application of the test article to the anterior surface of the eye.

Test Results: Under the conditions of the study, the test article is an irritant but not corrosive.

Inhalation Toxicity in Rats

Test Results: Under the conditions of the study, the test article is non-toxic.