

**METHOD OF REMOVAL OF CARBONYL COMPOUNDS ALONG WITH ACID
GASES FROM CRACKED GASES IN ETHYLENE PROCESS**

TECHNICAL FIELD OF THE INVENTION:

5 The present invention generally relates to a method of removing undesired by-products from pyrolytic cracking of hydrocarbons. The invention specifically relates to a method for removal of acetaldehyde and other carbonyl compounds along with other acidic gases like H_2S and CO_2 that are formed when cracked gasses enter a caustic tower or an amine unit within an ethylene plant, where the cracked gases are produced in a pyrolysis
10 heater during the pyrolytic cracking of hydrocarbons.

BACKGROUND OF THE INVENTION:

 In pyrolytic cracking operations, feedstock such as ethane, propane, naphtha, kerosene, gas oil, fuel oil and the like undergo "cracking," i.e. the removal of hydrogen, to form unsaturated hydrocarbons. Pyrolytic cracking also tends to produce oxygenated
15 hydrocarbons, including carbonyl compounds such as acetaldehyde. In a typical operation, the cracked effluent stream is quenched, fractionated and compressed. Acidic contaminants such as hydrogen sulfide, carbon dioxide and mercaptans are then typically removed from the effluent.

 During the operation of scrubbing these gases with caustics or amines, some
20 oxygenated compounds are removed. At the same time, however, the basic conditions in the scrubber tend to cause base-induced condensation reactions of the carbonyl compounds, including aldehydes (e.g., acetaldehyde) and/or ketones, which in turn result in the formation of polymers. These polymers are deposited on the internal surfaces of the scrubber. As the mass of polymer grows, it leads to fouling and can eventually obstruct the flow of liquids
25 through the system. This is undesirable, as the operating system must be shutdown for a significant amount of time in order to remove the deposited polymer and clean the equipment.

In the past, polymerization of oxygenated compounds, such as carbonyl-containing organics in basic solutions, has been prevented by adding amine compounds such as hydroxylamine hydrochloride, hydroxylamine sulfate, hydrazine, carbohydrazides and the like. Several patents relate to methods of inhibiting carbonyl fouling.

5 U.S. Pat. No. 4,673,489, granted to Roling, discloses using hydroxylamine and its salts of hydrochloric acid and sulfuric acid to inhibit polymer formation caused by condensation reactions of aldehydes contained in caustic scrubber units. One disadvantage of the method is that the additive has to be used in almost molar proportion.

U.S. Pat. No. 4,952,301, granted to Awbrey, discloses using ethylenediamines with
10 the molecular formula $\text{NH}_2(\text{CH}_2\text{CH}_2\text{NH})_x\text{H}$ where x is an integer ranging from 1 to about 10 to inhibit carbonyl based fouling, particularly aldehyde fouling, that often occurs during caustic scrubbing of liquid or gas phase hydrocarbon streams in the base wash unit.

U.S. Pat. No. 5,264,114, granted to Dunbar, discloses the use of amine compounds to inhibit the deposition of foulants during caustic washing of the hydrocarbon gases
15 contaminated with the carbonyl compounds which comprises of treating the said hydrocarbon gases with an aqueous amine solution wherein the said aqueous amine solution comprises water and an amine compound having a concentration range of 2 ppm to about 5000 ppm and wherein the said amine compound is selected from a group of organic compounds of the formula RNH_2 and R_2NH wherein the R is selected from the group of alkyl or aryl groups.

20 U.S. Pat. No. 5,160,425, granted to Lewis, discloses Carbohydrazide as useful for inhibiting polymeric fouling deposits during the caustic scrubbing of pyrolytically-produced hydrocarbons contaminated with oxygen-containing compounds.

U.S. Pat. No. 5,288,394, granted to Lewis et al., describes and claims a method of inhibiting formation of polymeric fouling deposits during the caustic scrubbing of a
25 hydrocarbon stream contaminated with oxygenated compounds with a basic washing solution

having pH greater than 7 comprising: adding to said hydrocarbon stream a sufficient amount of a compound containing at least one hydrazide compound for inhibiting formation and deposition of fouling materials.

U.S. Pat. No. 5,194,143, granted to Roling, describes and claims a method for
5 inhibiting the formation of polymeric based fouling deposits during the basic washing of olefins containing hydrocarbon contaminated with oxygenated compounds comprising about 1 to 10,000 parts per million acetoacetate ester compound having the formula $\text{CH}_3\text{COCH}_2\text{C}_x\text{H}_y$, where x is an integer from about 1 to about 8 and y is an integer from about 3 to about 17.

10 U.S. Pat. No. 5,220,104, granted to McDaniel et al., discloses the use of percarbonate salts for the same purpose.

U.S. Pat. No. 5,770,041, granted to Lewis et al., describes the use of certain aldehydic compounds without alpha hydrogen atoms or non-enolizable aldehydes like formaldehyde, glyoxal, etc. as aldol inhibitor, but again in this case the said inhibitor has to be used in at
15 least thrice the molar ratio per mole of carbonyl species.

U.S. Pat. No. 5,714,055, granted to Lewis et al., discloses the use of certain organic amine inhibitors like sulfanilic acid for inhibiting the aldol condensation in extremely severe fouling conditions, but this patent does not disclose the use of said inhibitor for dissolving the polymer once made.

20 The prior art systems treat caustic towers with an injection of a compound to inhibit the aldol condensation mechanism. In order to inhibit aldol condensation, the prior art systems mostly use additives that are organic in nature and contribute to chemical oxygen demand for caustic used in the scrubbing process. In addition, the prior art additives typically require that additive to reactant molar ratios be of at least 1:1 for effective performance.

25 Further, the adducts of high molecular weight polymers with these compounds tend to be

insoluble in the basic system. Thus, the prior art additives are ineffective for the purposes of maintaining unobstructed flow through the system and reducing significant maintenance time for removing polymer deposits and cleaning the equipment.

A current practice in the industry is to treat the weak caustic with gasoline or another aromatic fraction in order to remove the polymers before sending it to the spent caustic oxidation unit, in order to prevent fouling there. The resulting gasoline-containing stream causes disposal and operational problems, however. Likewise, routing the gasoline-containing stream to other operating units can cause problems due to the presence of the caustic, as it may effect pH, catalyst and reaction parameters.

Another current practice in the industry is to treat the caustic tower with organic additives, and despite the various advances in the art it remains desirable to provide an alternative method to improve the performance of this particular unit in the industry. There have also been shortcomings when any of these additives have been used concurrently to provide a synergistic effect in such systems.

Hence, it is desirable to provide a method for preventing fouling that does not create problems in equipment downstream of the scrubber and that does not pose significant environmental problems.

SUMMARY OF THE INVENTION:

In one aspect of the present invention, there is provided a method for inhibiting and dissolving polymeric deposits on the internal surfaces of a caustic wash unit system in a hydrocarbon cracking process wherein said deposits result from polymerization of at least one component contained within a feed stream of said caustic wash unit system, comprising the step of: introducing into said stream an effective amount of a combination including: (a) an inorganic salt of dithionite; and (b) a α [[n]] caprolactam, a sulfanilic acid or an [[6-]]amino caproic acid; wherein said effective amount of the combination is present in a molar ratio of inorganic salt of dithionite to caprolactam, sulfanilic acid or caproic acid of from 1:0.17 to 1:1.5 and wherein the combination inhibits the polymerization and dissolves said polymeric deposits.

One embodiment of the present invention discusses a method of using the so caustic/amine scrubber to scavenge acidic gases like H_2S and CO_2 , and additionally scavenge carbonyl compounds without posing any polymerization problems. Another embodiment of the present invention includes a method for scavenging oxygenated hydrocarbons without posing polymerization problems and without interfering with plant operations or with the operation of the individual process units.

One embodiment of the present invention includes a method that provides additional advantages of reducing the concentration of oxygenated hydrocarbons, particularly carbonyl compounds, in equipment and in product streams. Yet another embodiment of the present invention includes a method for inhibiting oxygenated hydrocarbon fouling that does not
5 interfere with overall plant operations or operations of the individual processes. The method in this embodiment provides the additional advantage of reducing the concentration of oxygenated hydrocarbons, particularly carbonyl compounds, in equipment and streams. An alternative embodiment of the present invention includes use of certain inorganic salts, (e.g. alkali metal salts of oxo acids of sulfur, alkali metal salts of acids of lactam, alkali metal salts
10 of acids of sultam, alkali metal salts of amino acids, alkaline earth metal salts of acids of sultam, alkaline earth metal salts of acids of amino acids, lactam, sultam, amino acids, and combinations thereof) that prevent the polymer formed by aldol condensation and further dissolve said polymer. The dissolution is observed in synergistic compositions.

Also, the present invention can be used along with caustic in the caustic tower, in that
15 the invention can be premixed with the caustic used for making the scrubbing solution.

BRIEF DESCRIPTION OF THE DRAWINGS:

Figs. 1A and 1B depict chemical compounds useful in the present invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS:

The present invention includes a method for inhibiting and dissolving the polymeric
20 deposits formed in caustic or alkaline scrubbers which are used for scrubbing acidic gases such as carbon dioxide and hydrogen sulfide from the effluent streams formed during the pyrolytic cracking of hydrocarbons such as naphtha, ethane, and propane. The cracking operations also produce oxygenated compounds such as vinyl acetate or acetaldehyde, which undergo polymerization under the alkaline conditions in the scrubber. Upon hydrolysis under

alkaline conditions, vinyl acetate releases acetaldehyde which contributes further to the buildup of polymeric deposits

One embodiment of the present invention includes a method wherein certain inorganic salts like sodium dithionite, sodium metabisulphite, and sodium bisulphate are used to mitigate fouling. Said inorganic salts are blended with aliphatic amino acids (including but not limited to 6-amino caproic acid) to mitigate the effects of polymerization in the system in synergistic combination. The blends of inorganic salts and aliphatic amino acids, particularly 6-amino caproic acid, not only prevent but also dissolve the polymers formed by the aldol condensation described above.

Another embodiment of the present invention includes a method wherein a combination of inorganic salts and certain lactams (including but not limited to epsilon caprolactam (molecular weight 113)) is used to mitigate the effects of polymerization in the system. The blend of the inorganic salt and caprolactam not only prevents but also dissolves the polymers formed by the aldol condensation described above.

In one embodiment of the present invention, when amino acids or lactams are used along with the inorganic salts, particularly sodium dithionite, they react with both the low and high molecular weight polymers such that the reacted adduct is soluble in the caustic solution. Thus, the amino acid and the inorganic salts in synergistic ratio solublize the polymers formed and prevent precipitation and fouling of the equipment. The present additives have the dual advantage of working as polymerization inhibitors by reacting with acetaldehydes as well as solublizing any existing polymers by reacting with them.

In one embodiment of the present invention, amino acids that are particularly useful include but are not limited to 6-amino acids such as the amino hexanoic acid made from epsilon caprolactum, glycine, or taurine, or any compound having one of the structures as shown in Figs. 1A and 1B. Also suitable are the derivatives, isomers, and inorganic or

organic salts of these compounds. These structures are representatives of only some embodiments of the present invention, however one skilled in the art will recognize that modifications to the embodiments may be made without departing from the scope of the claimed invention.

5 These said compounds, described in the preceding paragraph, are effective polymerization inhibitors for aldol condensation reactions. For the purposes of this invention, an acetaldehyde polymer may be defined as having 2 or more repeating units of acetaldehyde. These said compounds are effective scavengers for carbonyl compounds found in any hydrocarbon stream. Said compounds are also effective polymerization inhibitors for
10 aldol condensation reactions, as well as agents for solubilizing any polymers that may already have been formed by that mechanism.

 In one embodiment of the present invention, the inorganic salts may be added to the alkaline scrubber in an amount representing a molar ratio of carbonyl to inorganic salt is from about 1:0.01 to about 1:25 mole. Preferably the inorganic salt is added to the alkaline
15 scrubber in an amount representing a molar ratio of carbonyl to inorganic salt from about 1:0.05 to 1:0.005.

 In another embodiment of the present invention, the amino acid and the previously mentioned inorganic salts may be added to the alkaline scrubber in an amount representing a molar ratio of carbonyl to the mixture of amine and the inorganic salts is from about 1:0.01 to
20 about 1:25 mole. Preferably the mixture of amino acid and the inorganic salt is added to the alkaline scrubber in an amount representing a molar ratio of carbonyl to mixture from about 1:0.05 to 1: 0.005

 In yet another embodiment of the present invention, the lactam and the previously mentioned inorganic salts may be added to the alkaline scrubber in an amount representing a
25 molar ratio of carbonyl to the mixture of lactam and the inorganic salts from about 1:0.01 to

about 1:25 mole. Preferably the lactam and the inorganic salts are added to the alkaline scrubber in amount representing a molar ratio of carbonyl to lactam and the inorganic salts from about 1:0.5 to 1:0.25

In one embodiment of the present invention, salt of an amino acid or pure amino acid
5 or combinations thereof are added either as neat product or as an aqueous solution containing 0.05 to greater than 60 weight percent of the amino acid. In one embodiment, 18 weight percent of amino acid is used.

In one embodiment of the present invention, the lactam can be added either as neat product or as an aqueous solution containing 0.05 to greater than 60 weight percent of the
10 amino acid, with 18 or 38 weight percent preferred.

In yet another embodiment, the preferred amount of additive ranged from 0.5 to 1,000,000 parts of inhibitor per one million parts of the aqueous scrubbing medium used in the caustic wash system. Preferably, 25 to 200 ppm of additive was used.

The following Examples are merely illustrative of some embodiments of the present
15 invention and the manners in which it can be performed, and are not intended to limit the scope of the claimed invention in any way.

Example 1

To a clean four necked round bottom flask, equipped with a thermometer, stirrer and condenser, caprolactum (18 g, 0.1593 mole), sodium hydroxide (7 g, 0.175 g) and 75.0 g
20 water were added. The mixture was well agitated and heated to 105°C to 120°C for a period of six hours. Small samples were periodically withdrawn and checked for conversion using HPLC. The conversion of epsilon caprolactum to six amino hexanoic acid was greater than 75%.

Example 2

20 ml of 10% NaOH solution was added to a 50 ml stoppered conical flask. A desired inhibitor in solution or in solid form was then added, followed by the addition of 1 ml vinyl acetate. The mixture is shaken well and kept in an oven for 24 hrs at 55°C. One blank run was prepared wherein all reagents except the inhibitor were added. At the end of 24 hours the contents of the flask were visually checked for clarity or any deposits, and UV readings were measured. The following results were obtained as shown in Table 1.

Table 1

The following results were average readings from two to three identical runs with the same composition and reaction parameters.

Expt. No.	Compounds	gms	Mole Ratio	% Transmittance at 800 nm	Absorbance at 720 nm	Observation
1	Blank	nil	nil	0.5	2.5	Red hazy liquid with precipitate
1	Sodium dithionite	0.2075	0.125	68.5	0.2575	Red slightly hazy liquid
2	Sodium dithionite	0.4715	0.250	89.55	0.0475	Red clear liquid
3	Sodium dithionite	0.943	0.5	90	0.042	Faint red clear liquid
4	Sodium dithionite	1.886	1.0	80.35	0.09	Colorless liquid
5	Sodium metabisulphite	0.1281	0.0625	0.466	2.54	Red hazy liquid
6	Sodium metabisulfite	0.2562	0.125	80.7	0.179	Red clear liquid
7	Sodium metabisulfite	0.549	0.25	86.4	0.113	Red clear liquid
8	Sodium metabisulfite	2.089	1.0	87.3	0.066	Red clear liquid
11	Sodium bisulfite	0.140	0.125	2.8	1.80	Hazy red liquid
12	Sodium bisulfite	0.338	0.30	86.1	0.133	Red clear liquid
13	Sodium bisulfite	0.563	0.50	86	0.1035	Red clear liquid
14	Sodium bisulfite	1.127	1.0	89.1	0.092	Red clear liquid

17	Sodium sulfite	0.170	0.125	0.35	2.653	Red hazy liquid
18	Sodium sulfite	0.682	0.5	83.6	0.130	Red clear liquid
19	Sodium sulfite	1.365	1.0	89.2	0.08	Red clear liquid
20	Sodium sulfate	1.539	1.0	5.9	1.904	Hazy liquid with gummy polymer
21	Sodium hydrogen sulfate	1.496	1.0	4.4	1.332	Same as above

Example 3

20 ml of 10 % NaOH solution was pipetted into a 50 ml stoppered conical flask. To this was added 1 ml of vinyl acetate solution. The mixture was shaken well and kept in an oven for 15 minutes. During this period, the vinyl acetate was hydrolyzed and polymerized to form insoluble products. After 15 minutes the desired amount of inhibitor was added. One control sample was prepared without inhibitor. The flask was shaken well and kept in an oven for 24 hours. After 24 hours the flask was checked visually for clarity and any deposits. In some cases UV transmittance was measured for comparison. The results are shown in

10 Table 2.

Table 2: After Polymerization

Expt No.	Compounds	gms	Moles	Moles of	Total Moles	% Transmittance at 800nm	Absorbance at 720 nm	Observation
1	blank	nil	nil	nil	nil	0.5	2.5	Red turbid liquid with polymer particles
2	Sodium Dithionite	0.943	0.5	-----	0.5	62.5	0.202	Yellow clear liquid with few particles
3	Amino caproic acid	0.125		0.087	0.087	0.5	2.709	Same as above
4	Sodium Dithionite + Amino caproic acid	0.943 0.125	0.5	0.0879	0.5879	77.05	0.1125	Red clear transparent liquid

5	Sodium dithionite + Example 1	0.943 0.3ml	0.5 0.087		0.5879	85.7	0.07	Red clear transparent liquid
6	caprolactum	0.367 3	0.3		0.3	11.4	1.095	Hazy red liquid with particles
7	Sodium dithionite + caprolactam	0.943 0.367 3	0.5	0.3	0.8	69.7	0.171	Clear red liquid with few particles

Table 3: Before Polymerization

Expt . no	Compounds	gms	Moles of	Moles of	Total moles	% transmittance at 800nm	Absorbance at 720 nm	Observation
1	Sodium Dithionite		0.1	-----	0.1	18.5	0.842	Red hazy liquid
2	Amino caproic acid	0.0372	-----	0.026	0.026	0.3	2.571	Closer to blank
3	Sodium Dithionite + Amino caproic acid	0.1886 0.0372	0.1	0.026	0.126	82	0.183	Red clear transparent liquid
4	Sodium dithionite + Example 1	0.1886 0.09ml	0.1	0.026	0.126	81.0	0.210	Red clear transparent liquid
5	Sodium dithionite + sulfanilic acid	0.1886 0.3	0.1	0.160	0.260	86.7	0.1195	Red clear transparent liquid
6	Sulfanilic acid	0.30		0.160	0.160	0.2	2.872	Red brown hazy with particles
7	caprolactum	0.3673		0.3	0.3	0.4	2.783	Dark red slight hazy liquid with some dispersed particles
8	Caprolactum + sodium dithionite	0.1836 0.1886	0.1	0.15	0.250	82.9	0.176	Red clear transparent liquid

9	Sodium metabisulfite + sodium dithionite	0.1853 0.1866	0.1	0.09	0.190	93.3	0.067	Faint Red clear transparent liquid
10	Sodium dithionite + Amino caproic acid	0.1132 0.0888	0.06	0.0625	0.123	81	0.285	Red clear transparent liquid
11	Amino caproic acid	0.0888		0.0625	0.0625	0.3	2.872	Same as blank

The basic wash systems in which the present treatments were useful for inhibiting fouling include amine acid gas scrubber and caustic wash systems.

Example 4: Caustic Solution Stability

0.3 mole strength of sodium dithionite was prepared in 10 % NaOH solution. The performance of this sodium dithionite solution was tested periodically. To 20 ml of the solution, 1 ml vinyl acetate was added and shaken well. The flask was kept in the oven at 55°C for 24 hrs. The details of the result are listed in Table 4.

Table 4: Caustic Solution Stability

Sr. No.	Hours	% Transmittance at 800 nm	Absorbance @ 720 nm	Observation
1	24 hrs	90.3	0.122	Red clear transparent liquid
2	192	85.3	0.145	Red clear transparent liquid
3	240	87.9	0.140	Red clear transparent liquid
4	360	90.9	0.129	Red clear transparent liquid
5	480	87.3	0.142	Red clear transparent liquid

Example 5: Sodium Metabisulfite

0.2 mole strength of sodium dithionite was prepared in 10 % NaOH solution. The performance of this sodium dithionite solution was tested periodically. To 20 ml of the solution, 1 ml vinyl acetate was added and shaken well. The flask was kept in the oven at 55°C for 24 hrs. The details of the result are listed in Table 5.

Table 5: Sodium Metabisulfite

Sr. No.	Hours	% Transmittance at 800 nm	Absorbance @ 720 nm	Observation
1	24 hrs	90.7	0.095	Red clear transparent liquid
2	72	90.8	0.109	Red clear transparent liquid
3	168	90.3	0.105	Red clear transparent liquid
4	216	88.7	0.118	Red clear transparent liquid
5	336	90.4	0.116	Red clear transparent liquid

While the present invention has been described herein in terms of various
embodiments, one of ordinary skill in the art will recognize that modifications to the
5 embodiments can be made without departing from the scope of the claimed invention.

CLAIMS

1. A method for inhibiting and dissolving polymeric deposits on the internal surfaces of a caustic wash unit system in a hydrocarbon cracking process wherein said deposits result from polymerization of at least one component contained within a feed stream of said caustic wash unit system, comprising the step of:

introducing into said stream an effective amount of a combination including:

- (a) an inorganic salt of dithionite; and
- (b) a[[n]] caprolactam, a sulfanilic acid or an [[6-]]amino caproic acid;

wherein said effective amount of the combination is present in a molar ratio of inorganic salt of dithionite to caprolactam, sulfanilic acid or caproic acid of from 1:0.17 to 1:1.5 and wherein the combination inhibits the polymerization and dissolves said polymeric deposits.

2. The method according to claim 1 wherein said combination includes an inorganic salt of dithionite and [[6-]]amino caproic acid.

3. The method of claim 1, wherein the amino acid comprises amino caproic acid derived from caprolactum.

4. The method of claim 1, wherein the component contained within the feed stream is a carbonyl compound.

5. The method of claim 4, wherein the combination is introduced into the feedstream in a molar ratio of inorganic salt to carbonyl compound of from about 1:0.005 to about 1:25.