

# Chemical Control of Produced Water Solids

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## **ABSTRACT**

Dithiocarbamates (DTCs) are thorough fast-acting water clarifiers. Data has been presented which showed that DTCs function primarily by becoming insoluble. Data will be presented to show that DTCs also function by breaking reverse emulsions through complexation. Free oil adheres to this in-situ insoluble material some of which is iron sulfide ( $\text{Fe}_x\text{S}_y$ ). Iron sulfide is always a concern because it can lead to increased corrosion, equipment problems, injection well plugging and decreased water quality. Control of iron sulfide solids in produced water clarification systems by controlling the DTC use rate is difficult because of system upsets and production surges. The low level use of an additive in the dithiocarbamate formulation has controlled for many years the iron sulfide solids associated with the application of DTCs in the clarification of oilfield produced waters. However DTCs hydrolyze at low pH and with some DTCs this hydrolysis can produce another type of solid precipitate. This paper will demonstrate that although DTC clarifiers are robust, care must be taken when they are used in low pH or sour systems.

## Historical and Background

The use of DTC water clarifiers has been presented in the literature.<sup>1-3</sup> Their mode of action has also been presented<sup>4</sup>. Dithiocarbamates are strong chelaters of iron cations. But strictly speaking, iron does not have to be present for a DTC clarifier to function because a DTC floc has been observed in the presence of other transition metal ions; for example, Hg, Ag, Cu, Ni, Co, Pb, Cd, Zn, Mn and Fe. The use of an additive in DTC water clarifiers to chemically control the nature of the solids found in produced water system has been presented in the literature<sup>5</sup>. Their efficacy in preventing uncontrollable solids when using DTC type water clarifiers is also protected by patents<sup>6</sup>.

Reverse emulsions are typically caused by the carboxylic acids present in crude oil. When the crude oil meets water, a portion of these carboxylic acids partition to the aqueous phase. At pH = 7, the carboxylic acids become salts. As a sodium salt the compound is soluble but as a calcium salt many of these acids are not truly water soluble despite significant water-loving tendencies<sup>7</sup>. The traditional effective quaternary amine will complex with these carboxylic acid salts to make a new complex which is oil soluble. Without the emulsifying agent residing at the oil/water interface, the reverse emulsion breaks. This behavior has been reported for inorganic clarifiers<sup>8</sup>. The performance of the traditional amine water clarifier is known to vary with total dissolved solids (TDS), temperature, agitation and the presence of other chemicals (for example, corrosion inhibitors).

The proposed mechanism of clarification with a DTC is thought to be different from that of a conventional water clarifier. It is thought that a DTC reacts with metal ion (iron) in the system to produce a metal ion complexed flocculant which is highly efficient at carrying out dispersed oil<sup>2</sup>. In addition, any precipitation which occurs in the presence of emulsified oil will remove it.

## Results and Discussion

Although when DTCs are applied to fresh water a clear solution will typically result, their solubility is a powerful tool in clarifying produced waters because not all DTCs produce the same amount of floc or clarify to the same extent. The performance of a DTC water clarifier will also vary with TDS, temperature, agitation and the presence of other chemicals. Table 1 shows four Baker Petrolite products using 3 DTCs with varying solubilities in typical field waters. So as an alternative to the original mechanism it is now proposed that DTCs operate via a complexation mechanism typical of most clarifiers; by breaking the reverse emulsion then removing any free oil.

Table 1 - DTC Variations

DTC Variations	Behavior in Fresh water	Behavior in 10% brine*	Behavior in 20% brine*
A	Soluble	Soluble	Soluble
B	Soluble	Dispersible	Dispersible
C	Soluble	Dispersible	Floc
C w/ additive	Dispersible	Dispersible	Dispersible

To prove this theory a simple solubility/extraction experiment was run. DTC A exhibits no "oil solubility" under normal conditions but when equal weights of 2-ethylhexanoic acid calcium salt and DTC A were dissolved in chloroform and then extracted with deionized water, the dithiocarbamate was seen by proton nuclear magnetic resonance (PNMR) only in the organic phase. In addition, inductively coupled atomic plasma (ICAP) analysis of the aqueous phase gave indication of the formation of an oil soluble mixed calcium salt since sodium was found in the aqueous phase even though dithiocarbamate was not found. So the first step is an exchange of cations typical of a complexation mechanism (Equation #1). When clarifiers clean water via a complexation mechanism a less water soluble DTC will produce an even more oil soluble complex with a carboxylate salt. However if the clarifier is insoluble in water, the continuous phase, then it will not function or only poorly.

It has been observed that systems with soluble iron present tend to clarify with DTCs better than those without it. When DTCs are used in the field, black iron sulfide solids ( $Fe_xS_y$ ) are generated. Optimum performance is considered to be when a fine dispersion is formed because the micelles present will provide a surface where oil can agglomerate. To better understand this step some deposit analysis from a produced water DTC application was undertaken. A typical analysis of a deposit by thermal gravimetric analysis (TGA) followed by a qualitative x-ray fluorescence (XRF) elemental analysis is presented in Table 2. Iron sulfide ( $Fe_xS_y$ ) is found in the solids. Extraction of these solids with chloroform yields soluble material some of which is merely entrained oil but an FT/IR scan of chloroform extract also shows an unusual peak ( $\sim 2100\text{ cm}^{-1}$ ) that is typical of an isothiocyanate (Equation #3). Note that iron sulfide results with Equation #2. The formation of isothiocyanates is not due to thermal decomposition because a TGA (attached behind the references) shows that a DTC (as is in aqueous base) is stable at temperatures greater than 300F<sup>9,10</sup>. When a sample of DTC A is added to a solution of ferrous chloride in water, the same black solids form immediately and the same 2100  $\text{cm}^{-1}$  peak is found in the chloroform soluble fraction. An FT/IR of the insoluble material showed very few definitive peaks. This is expected with these molecules because C-S FT/IR peaks are not distinctive. Some of the solids appear to be the iron salt of the DTC by ICAP and % Schoeniger Sulfur determinations on the chloroform soluble fraction. It was assumed that measureable iron could only be due to the salt not to any insoluble iron sulfide (Equation #3). Chloroform is a better solvent than crude oil so under normal conditions seen in the field the products from Equation #2 or #3 are probably insoluble

and this property is why DTCs are so effective at removing any free oil. However, the ability to break the reverse in Equation #1 is what distinguishes one product from another.

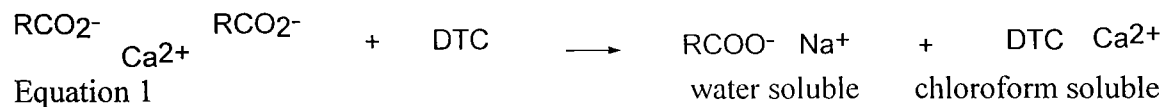


Table2 – Deposit Analysis Gulf Coast Wemco Float Cell

TGA	Wt%
Ignitables (organic/inorganic)	73
Non-ignitables, Ash	27
Chloroform soluble	35
Insoluble organics	38
Sodium chloride	12
Major minerals (calcium phosphate, barium sulfate, clay and silicon dioxide)	5
Iron sulfide	10
Lab Preparation	
Iron in chloroform soluble material	7

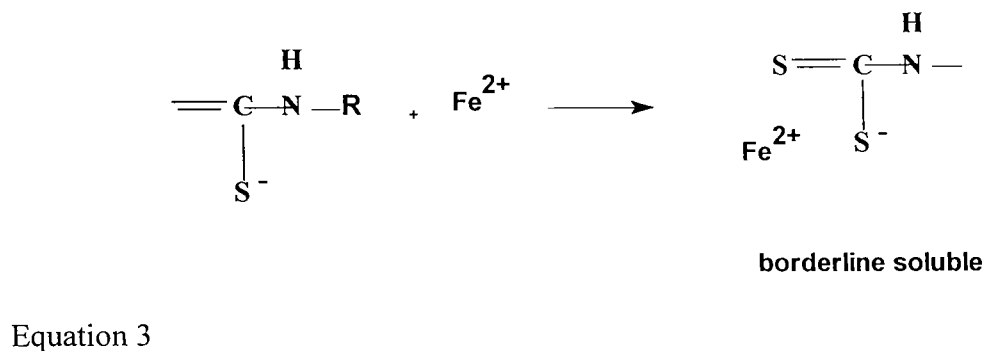
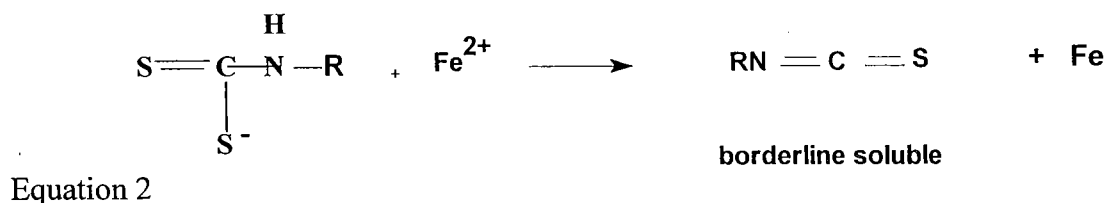
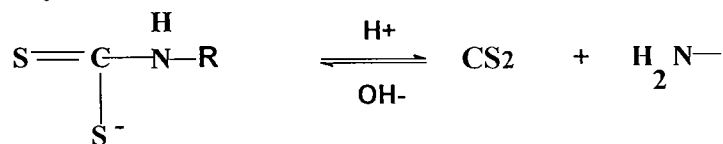


Table3 – Deposit Analysis Gulf Coast Overboard Water Line

TGA	Wt%
Ignitables (organic/inorganic)	23
Non-ignitables, Ash	77
Iron oxide	62
Silicon Oxide	15
Calcium phosphate	12
Sodium chloride	7
Major minerals (Iron sulfide, clay and others)	4

DTCs do not perform as well in sour fields as in fresh waters. When DTCs see low pH environments (~6) we tend to see solids more like those in Table 3. There is a much larger percentage of non-ignitable ash and a much smaller percentage of organic material. There is very little chloroform soluble material and there is no 2100 cm<sup>-1</sup> peak in the FT/IR. The ignitable weight loss has been attributed to moisture, phosphates or amines. The presence of amines was confirmed by a qualitative Nessler's reagent test. The instability of DTCs at low pH has been studied<sup>11-16</sup>. If a DTC is subjected to an acidic pH it will hydrolyze back to its starting materials and if hydrolysis occurs in acidic waters then the solubility of the DTC starting amine could become important.



Equation 5

Baker Petrolite has developed a method which can determine the activity of a DTC by potentiometric titration. This requires dissolving the sample (see method in appendix below) and then titrating with AgNO<sub>3</sub> (silver nitrate). Percent hydrolysis of a DTC in acid can also be measured by this titration. To study the effect that DTC structure has upon stability three different DTCs were held at pH = 6 then titrated one hour later. The data is presented in Table 4 and experimental details are in the appendix.

**Table 4 Equivalent Dithiocarbamate Activity**

Product	Equivalent Dithiocarbamate Activity (mEq DTC / g Product)	
	1,000 ppm-w Product Solution Not Acidified	1,000 ppm-w Product Solution pH = 6.0 (1 hour)
DTC A	3.69 (as is pH = 9.7)	3.35
DTC B	2.47 (as is pH = 10.7)	1.63
DTC C	2.56 (as is pH = 9.5)	1.56

The DTC B differs from DTC A and C in that it contains some sterically hindered 3° dithiocarbamate instead of all DTC as 2° dithiocarbamate. The results indicate that the product, DTC A, is the most stable to lower pHs because it exhibits the smallest change in apparent activity. Perhaps the added stability expected with DTC B is masked by the presence of some 2° dithiocarbamate also present. The two most recent references predict a mechanism dependent on the basicity of the starting amine<sup>15, 16</sup>. DTC A is built from the least basic amine. More work is required to better understand the impact that this has on hydrolytic stability. From a more practical viewpoint, hydrolysis could be significant depending on the residence time in the produced water system. If the pH is lower than 6 this rate of decomposition will even be faster. Some fields, high in CO<sub>2</sub>, have recorded pHs as low as 4. Based on data from the literature<sup>11</sup> (for diethyl DTC) a half-life of only thirty minutes at this pH was predicted. At pH 4, when faced with a loss in water clarifier performance, the typical course of action with DTC B or DTC C would be to increase the rate to compensate. But it is conceivable that this course of action would not improve the water and it could actually cause another type of solid build-up from the DTC amine backbone (Table 5). The solubility of these amines decreases with an increase in the brine concentration. Only DTC A amine remains soluble in 20% brine.

Oftentimes DTCs work in produced water systems when no other clarifier shows any activity. If there is no alternative clarifier and there is evidence of hydrolysis then attempts should be made to reduce the exposure to the acidic pH; for example, by moving the injection point closer to the float cell. Another approach would be to concurrently add a base to bring the system back to a more neutral pH.

Table 5 - Amine Backbone for DTC Variations

Amine Backbone for DTC Variations	Behavior in Fresh water	Behavior in 10% brine*	Behavior in 20% brine*
DTC A	Soluble	Soluble	Soluble
DTC B	Hazy	Insoluble	Insoluble
DTC C	Insoluble	Insoluble	Insoluble

## Conclusions

Iron sulfide is perhaps the most common solid found in the oilfield. Dealing with its presence in a production system is routine even before the addition of a DTC clarifier. DTC clarifiers find use in many produced water streams particularly those with soluble iron. They work through a complexation mechanism which breaks the reverse emulsion by exchanging the DTC sodium or potassium ions for (primarily) the calcium ion that had been associated with a carboxylate emulsifying agent from the crude oil. The DTC then becomes *borderline* insoluble. Free oil coats this surface and is removed. Their performance is nearly universal and so outstanding that DTCs find wide acceptance and application in spite of their tendency to make solids. However when the produced water systems are sour or acidic care must be taken to prevent DTC decomposition. Increasing the dosage rate to improve the water clarity may actually decrease the water clarity by formation of amine backbone solids. Low pH will result in hydrolysis of the DTC that could result in water insoluble material that could precipitate on water clarification equipment. There are ways that one can still effectively clarify these acidic waters.

## REFERENCES

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- <sup>2</sup> "Offshore Produced Water Treatment Using Dithiocarbamate Water Clarifiers" Nace 1997 Southern Central Regional Conference presented by Danny Durham.
- <sup>3</sup> "The Prepared Mind," *Chemtech*, September, 1994, pp7-9.
- <sup>4</sup> "Heavy Metal Removal Using Dithiocarbamates," *Plating and Surface*, **1/82**, pp67-71.
- <sup>5</sup> "Alba Northern Platform, Produced Water System Improvements" SPE50737 presented at 1999 SPE International Symposium on Oilfield Chemistry held in Houston, TX, 16-19 February 1999.
- <sup>6</sup> US Patents: 4,855,060; 5,006,274; 5,152,927; 5,190,683; 5,247,087; 5,302,296;
- <sup>7</sup> Robert A. Grimm in a: *Journal of the American Oil Chemists' Society Monograph "Fatty Acids"* pp 218-235.
- <sup>8</sup> E. Matijevec et al., *J. Phy. Chem*, **66**, 111 (1962).
- <sup>9</sup> F. B. Zienty and R. C. Thielke, *JACS*, **67**, (1945)pp.1040-1041.
- <sup>10</sup> P. Lambrinos et al, *European Polymer Journal*, **10**, (1990) pp.1132-1135.
- <sup>10a</sup> Since DTC B is 38% active and TGA shows this percentage or greater at 270F we predict that DTC B is stable at 270F (attached data is on the last page).
- <sup>11</sup> A.E.Martin, *Anal. Chem*, **25**, 8 (1962), pp1260-1261.

<sup>12</sup> C.L. Chakrabarti et al., *Anal. Chem.*, **41**, 11 (1969) pp1441-1445.

<sup>13</sup> C.L. Chakrabarti et al., *J. Phy. Chem.*, **74**, 4 (1970) pp860-865.

<sup>14</sup> D. De Filippo et al., *J.Org.Chem.*, **38**, 3 (1973) pp560-563.

<sup>15</sup> Eduardo Humeres et al., *J.Org.Chem.*, **63**, 5 (1998); pp1598-1603.

<sup>16</sup> Eduardo Humeres et al., *J.Org.Chem.*, **64**, 6 (1999); pp1807-1813.

## Appendix

For a typical DTC product stability test, a 1,000 ppm-w Dithiocarbamate (DTC) product dilution was tested for DTC concentration by abstracting a 15 g aliquot, adding 60 mL of acetone and 1 mL of concentrated  $\text{NH}_4\text{OH}_{(\text{aq})}$ , then titrating for active dithiocarbamate using 0.0142 N silver nitrate on a Brinkmann 686 titrator equipped with silver billet electrode and a pH calomel reference probe. Identification of the proper inflection endpoint was aided by titrating sodium diethyldithiocarbamate trihydrate as a reference standard. DTC concentration was expressed as "Equivalent Dithiocarbamate" in terms of milliequivalents per gram of dissolved product sample and was derived through the relationship shown below.

$$[\text{Equivalent Dithiocarbamate}] = \frac{(V_1) * (N)}{(W_s)}, \text{ in milli-Equivalents / g product}$$

where  $V_1$  = Volume (mL) of  $\text{AgNO}_3$  titrant  
 $N$  = Normality of  $\text{AgNO}_3$  titrant  
 $W_s$  = Weight (g) of sample (product) in aqueous solution  
= (0.015 g for a 15 g aliquot of a 1,000 ppm-w

dilution)

This represented the concentration for the case of a non-acidified aqueous solution of the product. (DTC product solutions possessed pHs at or above 9.0.)

For the case of the product dissolved in an acidic water solution, a 60 g portion of the 1,000 ppm-w product dilution was mounted on a Mettler DL-21 titrator with a pH probe and stirrer attached. The Mettler titrator was programmed with a "pH-stat" program to monitor and control the product's solution at pH=6 for one hour. At the start of the program, the titrator sensed the high pH of the DTC product solution and automatically added small volumes of dilute nitric acid solution until the pH was below 6.0. When the solution's pH tended to rise above 6 over time, the titrator injected small doses of acid only as needed to maintain the solution pH just below 6. This proceeded for an hour where the titrator kept a running total of the dilute acid solution injected to the 60 g product solution. Afterwards, the acidified acid solution was removed from the Mettler DL-21 titrator and a 15 mL aliquot was taken, blended with 60 mL acetone and 1 mL concentrated  $\text{NH}_4\text{OH}_{(\text{aq})}$  solution, then similarly titrated for DTC concentration on the



Brinkmann 636 titrator. (The product sample weight,  $W_s$ , in the acidified 15 mL titrated aliquot was adjusted by ratio knowing the volume or weight of diluted nitric acid solution injected into the 60 g portion of the 1,000 ppm-w product solution.)

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Size: 14.1910 mg  
Method: SOLIDS  
Comment: UNDER AIR BLANKET

# TGA

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Operator: HAZEM  
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