

# Sweetening Process Foaming and Abatement Part II: Case Studies

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## **ABSTRACT**

It was established in part I, that the contaminants that cause amine solvent foaming were incorporated in the foam itself. A device was constructed that used a nonoxidizing gas to concentrate the foaming contaminants, separate the foamate from the amine, and collect it for discharge and analysis.

Part II of this study describes the field results from using this device in gas plant and refinery applications. Descriptions of the plant problems, and how the device performed in each case are reported.

## **SUMMARY OF PART I**

### **Part I Table of Contents**

Foaming Upsets are Expensive  
Maintaining Clean Solvents  
Foaming Under Plant Conditions  
Plant Responses to Foaming Upsets  
Foaming and Carryover Relationships  
Removing Only Foam Causing Contaminants  
SigmaPure System Applications  
Comparative Upset Economics  
Solvent Reclamation Units  
Conclusion

The first part of this study presented several fundamental facts and hypotheses about amine foaming. First, despite the fact that foaming costs were in the millions per year, and the causes well known, the problems persisted. Research on a widely applicable solution to foaming issues was slowed, in part, because the plants had methods for handling foaming problems on a short term basis, namely, adding antifoam, changing particle filters and activated carbon. None of these methods specifically targeted the actual foam causing agents. Further, the actual causative agents were not recognized, so abatement strategies varied from upset to upset. The result was a constant recurrence of foaming problems in sweetening plants, and a severe lack of basic information that would allow consistent and widely applicable abatement strategies.

To begin addressing the problem, it was generalized that any surface active contaminant would cause foaming if the mechanical environment were presented, e.g., gas, liquid, surfactant and turbulence. Recognizing that surfactants were actually responsible for foaming, all other contaminants being ancillary, gave a starting point for formulating a solution.

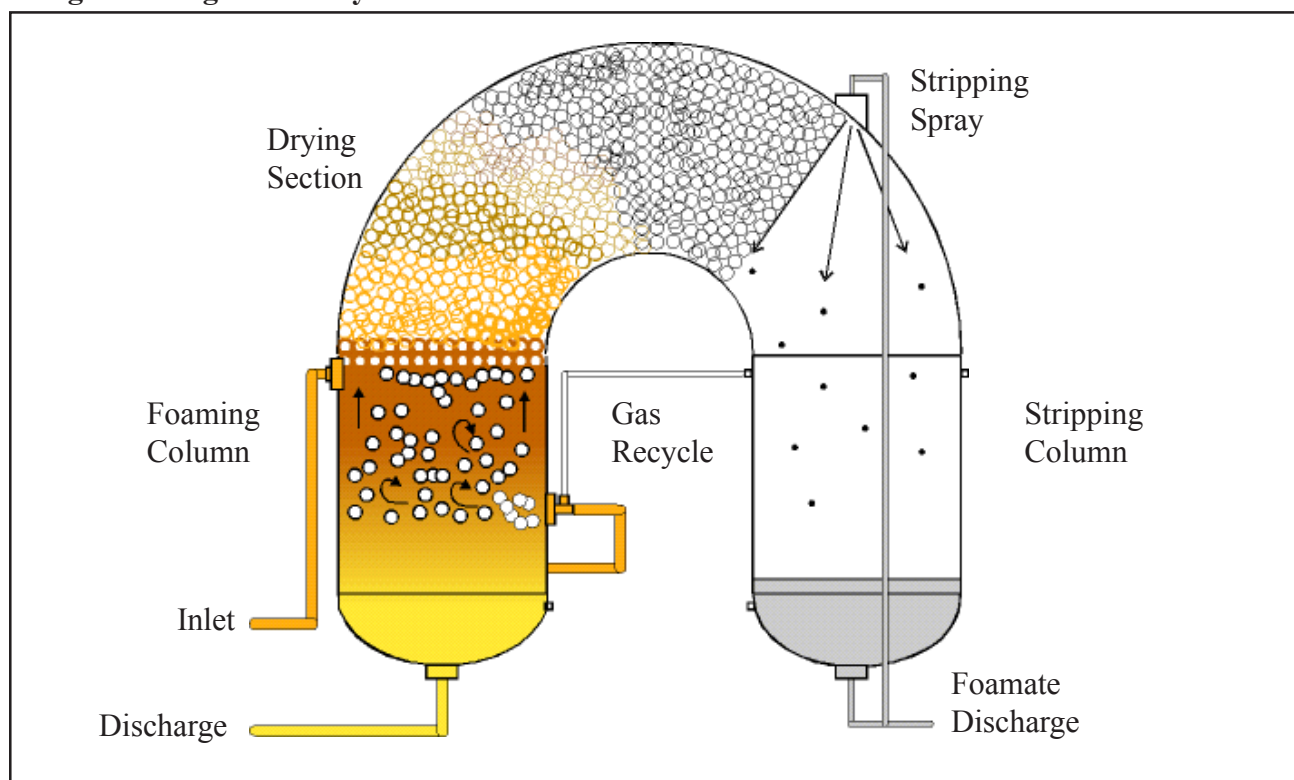
Surfactants naturally adsorb to the gas-liquid interfaces. This meant that the contaminating surfactants were incorporated in the bubble walls of the foam structure. The bubbles in the foam were not simply being formed in the froth above the trays or on the surface of packing, but rather started in the bulk solution. That is to say that the surfactants were being adsorbed and carried to the interface by the gas bubbles as they passed through the solution. The implications of this were even more significant than the formation of foam itself. Namely, the gas-liquid interface would be coated with surfactant as the gas passed through the bulk or pooled amine in the tower internal, and continued with the formation of stable foam. Since the bubble surface area represents the actual mass transfer area, the contaminating surfactants were probably having an affect on the solvent activity. Further research showed that in other industries gas to solvent mass transfer inhibition of up to 70% was not uncommon when surfactants were present in the liquid phase.

Surfactants could be soluble or insoluble, and were surface active, i.e., lowered solutions surface tensions at extremely low concentrations. Since the surfactant film in the bubble wall was so thin, i.e., a few nanometers to microns, a little contamination would form a lot of foam. This accounted for the surfactants' apparent invisibility in analyses. Being organic molecules also contributed to their lack of detection.

Common surfactants had very familiar chemistries, i.e., carboxylic acids, sulfonates, sulfates, and some alcohols just to name a few. The most probable sources for most of these contaminating surfactants were the sweetening solvents themselves, i.e., degradation products.

Recognizing the nature of the contaminants actually responsible for the formation of foam led to the development of a device for their separation. (see figure 1) The strategy was to "pre foam" the amine by introducing a cascade of nonoxidizing gas bubbles into the unit's foaming column. Any soluble or insoluble contaminant that participated in foam development would be incorporated in the foam structure formed at the bulk gas - liquid interface, and consequently separated from the amine. As the foam was displaced up the column into the drying section, clean solvent held in the structure would be allowed to drain back into the foaming column and recovered. The dry foam would be broken by the stripping spray. The spray droplets would coalesce the liquid fraction of the foam, and settle into the sump for recycling as spray or discharged as foamate. The released foaming gas would be recycled to the foaming column and used again.

**Figure 1. SigmaPure System**



With the cause defined, and the removal device conceptually designed, a procedure was needed for the identification of the surfactants. For this we turned to traditional analyses for organic compounds, i.e., gas chromatography and infra red spectroscopy. However, when the initial foamate samples were analyzed, the results were inconclusive. There was simply too much organic noise.

The contaminating surfactants were being masked by the other organic compounds in the foamate. We decided to further concentrate the surfactants by re-foaming the foamate and collecting the foam for analysis. This time we used FTIR to show the functional groups of the compounds present rather than the whole molecules. Although FTIR did clean up the results, more work remains to more fully define the contaminating surfactants.

## **INTRODUCTION TO CASE STUDIES**

There was a flurry of questions asked after making the concept and device public last year. Among those questions asked most frequently were:

- Will the system actually work?
- Is it solvent specific?
- Does it have an affect on the solvent?
- How long will the treatment last?
- What are the most common surfactants in amine systems?
- Will it eliminate the need for antifoam?

Most of these questions, and the host of others asked, would have to be answered in the field.

The following article reports the findings and observations while using the SigmaPure System in a variety of plants. The plants represented include Chemical, Natural Gas Processing, and Refining. The solvents treated in these cases included MDEA, DEA, and DIPA. The questions mentioned above are addressed at the end of the paper.

## CASE 1.0

This plant had been experiencing almost daily foaming upsets, and significant amine losses due to carryover. The plant was foaming when the SigmaPure System was installed.

Following electrical and mechanical inspections, the SigmaPure system was purged with nitrogen and brought on line. The SP unit tapped into the lean amine flow between one of two lean amine exchangers, and discharged into the absorber charge pump inlet. A flow rate of approximately 30 US gpm was established. This represented about 40% of the process flow.

**Figure 2.0 Case 1 Inlet, Treated Discharge, Foamate**



The SigmaPure unit was allowed to operate for approximately 1 hour before samples were taken. The picture in figure 1 shows the condition of the inlet and discharge amine. The foamate sample shown was taken at the end of the run.

## CASE 1 FOAMATE ACCUMULATION RATE

After 4 hours of operation, the liquid level in the stripping column began to slowly increase, indicating that the foamate was indeed being collected. Foamate accumulation rate was recorded with total amine treated. These data are shown in table 3.0. The system was operated for approximately 10 hours daily for 5 days, resulting in the collection of 6.19 gallons of concentrated foamate from 87,300 gallons treated.

**Figure 3.0. Case 1 Foamate Accumulation Rate**

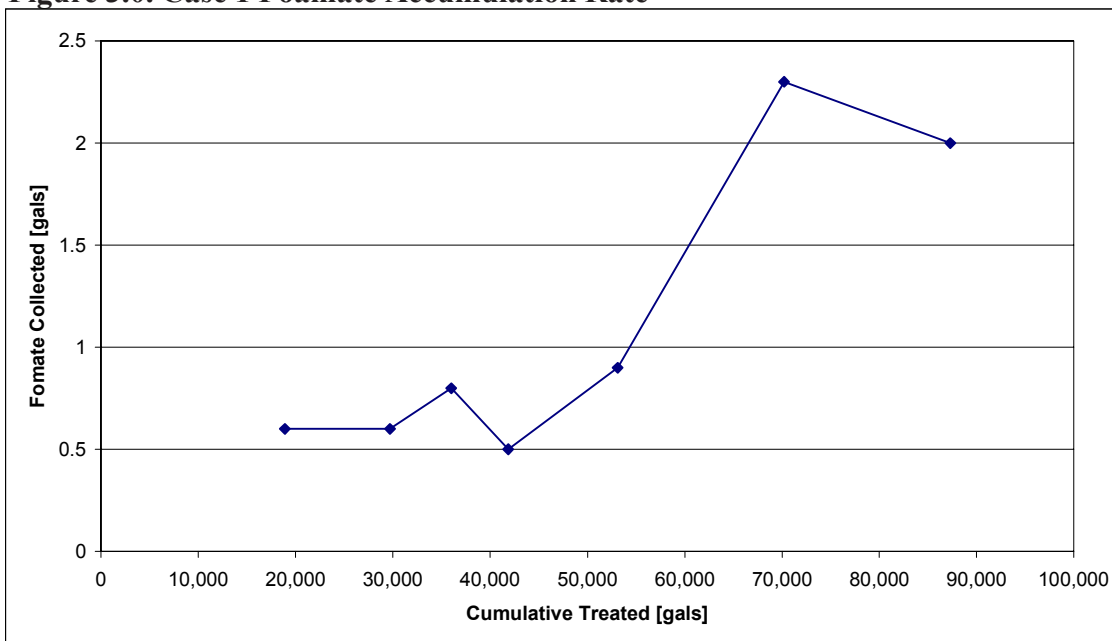


Figure 3 clearly shows that the foamate accumulation rate began to increase after the concentration of amine was increased. This indicated that surfactants were coming from either the make up water, the amine itself, or the associated vessels. There was no reported loss of solvent activity or absorber efficiency when the surfactants were removed from the recirculating amine, so the contaminants were probably not an intended amine fraction.

The surfactants contaminating the system made a dramatic jump between 50 and 70K gallons. The only change made in the plant during that time was a 15% increase in gas rate to the absorber. The differential pressure had reduced and remained steady for three days, so it was decided to increase the rate. The conclusions were obvious. The bulk of the foam causing contaminants were entering the system with the inlet gas, added to a small amount from the solvent make up system.

### CASE 1 PHYSICAL ANALYSIS

Although the plant's foaming problems had been stopped, the physical analytical data revealed a few more interesting pieces of the foaming puzzle. First, the make up water had a very high surface tension indicating that it wasn't the source of the make up contamination. This left the concentrated solvent, storage vessel, or piping as the potential sources for the surfactants. These were not investigated further because their contribution was considered extremely low.

The inlet amine's surface tension began to increase within a few hours of the SigmaPure's operation. The foaming tendency and breaktime of the discharge samples indicates that, with a fairly constant surfactant removal rate, the amount of inlet contamination was going down rapidly. This

**Table 1.0 Case 1 Physical Analysis**

Description	Surface Tension 122 F, [dyne/cm]	Foam Height 122 F, [mls]	Break Time 122 F, [sec]	Suspended Solids, [mg/l]
Initial Inlet	44.4	70	9	14.74
Discharge 1	47.6	20	2	2.08
Discharge 2	49.2	20	2	2.04
Discharge 3	51.3	10	1	1.02
Foamate 1	44.2	20	1	194.8
Foamate 2	42.6	60	15	139.2
Makeup Water	77.5	10	0	na

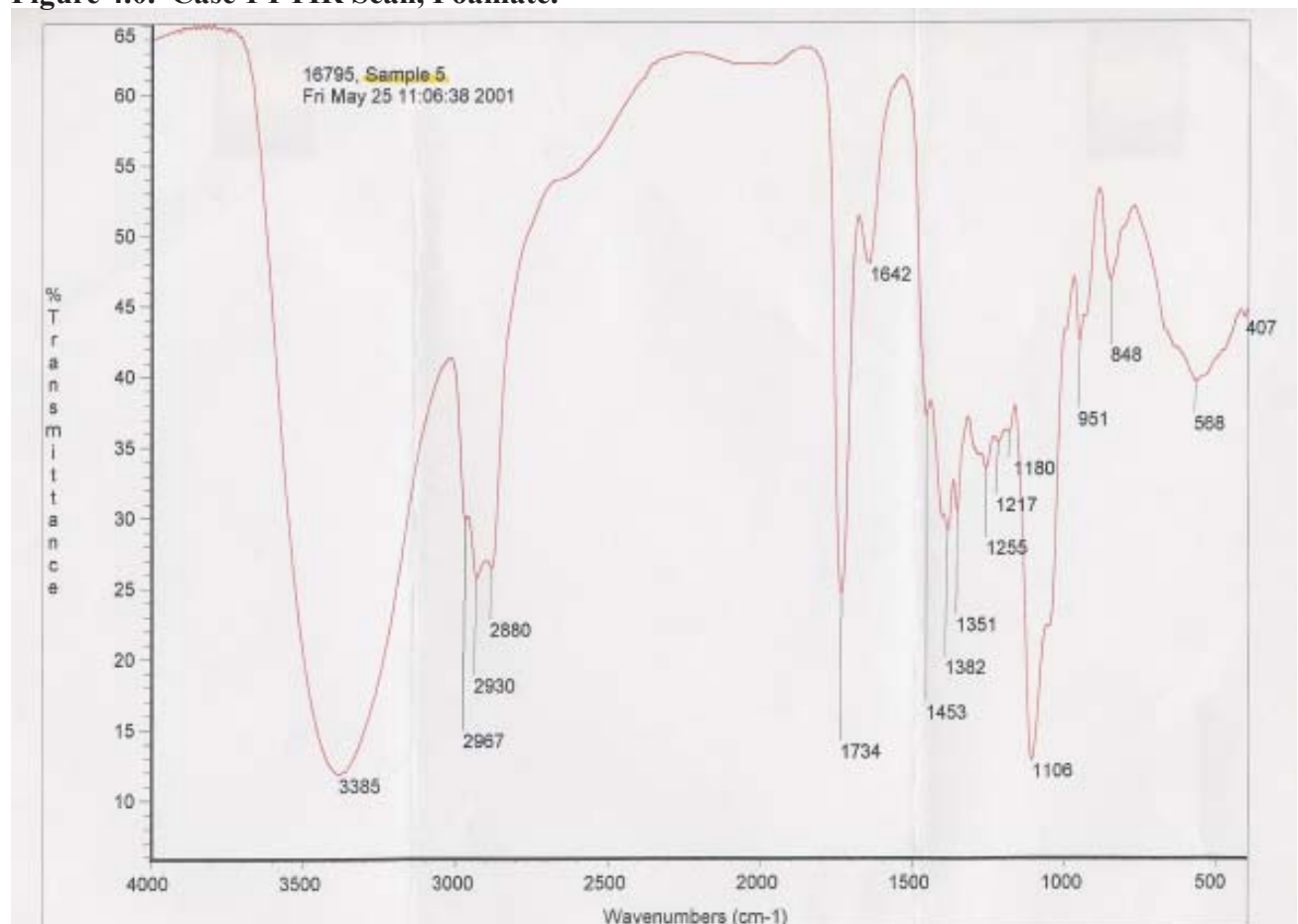
explains why the absorber differential pressure decreased and remained steady for the first time in months. Although it should have been predicted, one of the surprises was the total suspended solids concentration. Both the data and sample pictures show that the suspended solids readily associated themselves with the foam structure and were removed. This confirms that the solids, most of which were below the 5 micron level, play a significant role in foam stability. However, they also show that there is probably a solids/surfactant ratio above which the solids tend to stabilize the solvent, thereby reducing the foaming tendency (see Foamate 1 and Foamate 2, table 1).

### CASE 1 CHEMICAL ANALYSIS

Figure 4.0 shows the results of an FTIR scan of the foamate (twice foamed). Table 2.0 shows the identification of the peaks shown on the scan. The peaks represented the functional groups of the organics detected by the scan. Table 3.0 shows the breakdown, by % concentration, of the compounds identified. Breaking the data out in this manner made it easy to determine the most concentrated fractions of the foamate. It follows that the most highly concentrated compounds found in the foam would be those that were most responsible for its development. These are the compounds that were incorporated in the foam structure, therefore should be the foam causing agents.

In this case, short chain carboxylic acids, sulfonates, and ethoxylated alcohols were found to be the culprits. Previous analytical work performed by the plant identified the most probable foam causing contaminant to be glycols detected in the inlet gas. Obviously, this was not the cause of their foaming problems. Short chain carboxylic acids were most likely coming from amine degradation.

**Figure 4.0. Case 1 FTIR Scan, Foamate.**



**Table 2.0 Case 1 FTIR Scan Legend.**

Wave Number	Characteristic Compounds
3385	Water, Hydroxides, Amines Glycols
2967, 2930, 2880	CH <sub>2</sub> and CH <sub>3</sub> Aliphatic Hydrocarbon Chains
1734	Carboxylic Acids (Fatty Acids, Aldehydes, Ketones)
1642	Carboxylic (Fatty Acid Salts) and Amine Salts
1453	Aliphatic Hydrocarbons
1382	Aliphatic Hydrocarbons
1351	Amines
1255	Alkyl Sulfonates (Anionic Surfactants)
1217	Alkyl Sulfonates (Anionic Surfactants)
1180	Benzene and Xylene Sulfonates (Anionic Surfactants)
1106	Ethoxylated Alcohols (Non Ionic Detergents)
951	Glycols
848	Glycols
568	Aliphatic Hydrocarbons

Total Organic Compounds - 51,500 mg/l

**Table 3.0 Case 1 Foamate Constituents**

Compounds	Concentration [percent of total]
Short Chain Carboxylic Acids	20
Long Chain Carboxylic Acids	5
Total Amines	10
Aldehydes	5
Ketones	5
Sulfonates	20
Ethoxylated Alcohols	30
Glycols	5

It should be noted that these compounds are also associated with corrosion problems. The sulfonates were a by-product of H<sub>2</sub>S reacting with the amine. The ethoxylated alcohols were probably constituents of the antifoam being dosed by the plant, but could have been a sign of O<sub>2</sub> ingress. Glycols were playing a minor role, if any, in the plants foaming problem.

### CASE 1 CONCLUSIONS

The SigmaPure System successfully removed the surfactants from the plant's amine system. The effect was dramatic and positive. The SP unit removed the foam stabilizing solid particles along with the surfactant. Most of the solids removed were well below the removal range of the filters being used in the plant. There were no reports of negative effects to the amine's ability to treat the gas. On the contrary, the plant had been trying, unsuccessfully, to increase the amine concentration for several months. That change was made while the SP unit was on-line. The was also able to bring additional feed on-line, which increase the plant's throughput by a reported 15%. The plant did not have to add antifoam to the system for the duration of the run.

The analytical techniques used allowed the solvent to be characterized by surface tension for the first time. It also demonstrated the role suspended solids were playing in their foaming problem. Further, the surfactants contaminating the amine were segregated from the solvent and quantitatively

identified. This information allowed plant personnel to confidently formulate future abatement strategies.

We were also able to show, on a preliminary basis, that amine degradation products, the most common source for low molecular weight carboxylic acids in these systems, were acting as surfactants. As surfactants, they were removable by the SigmaPure System.

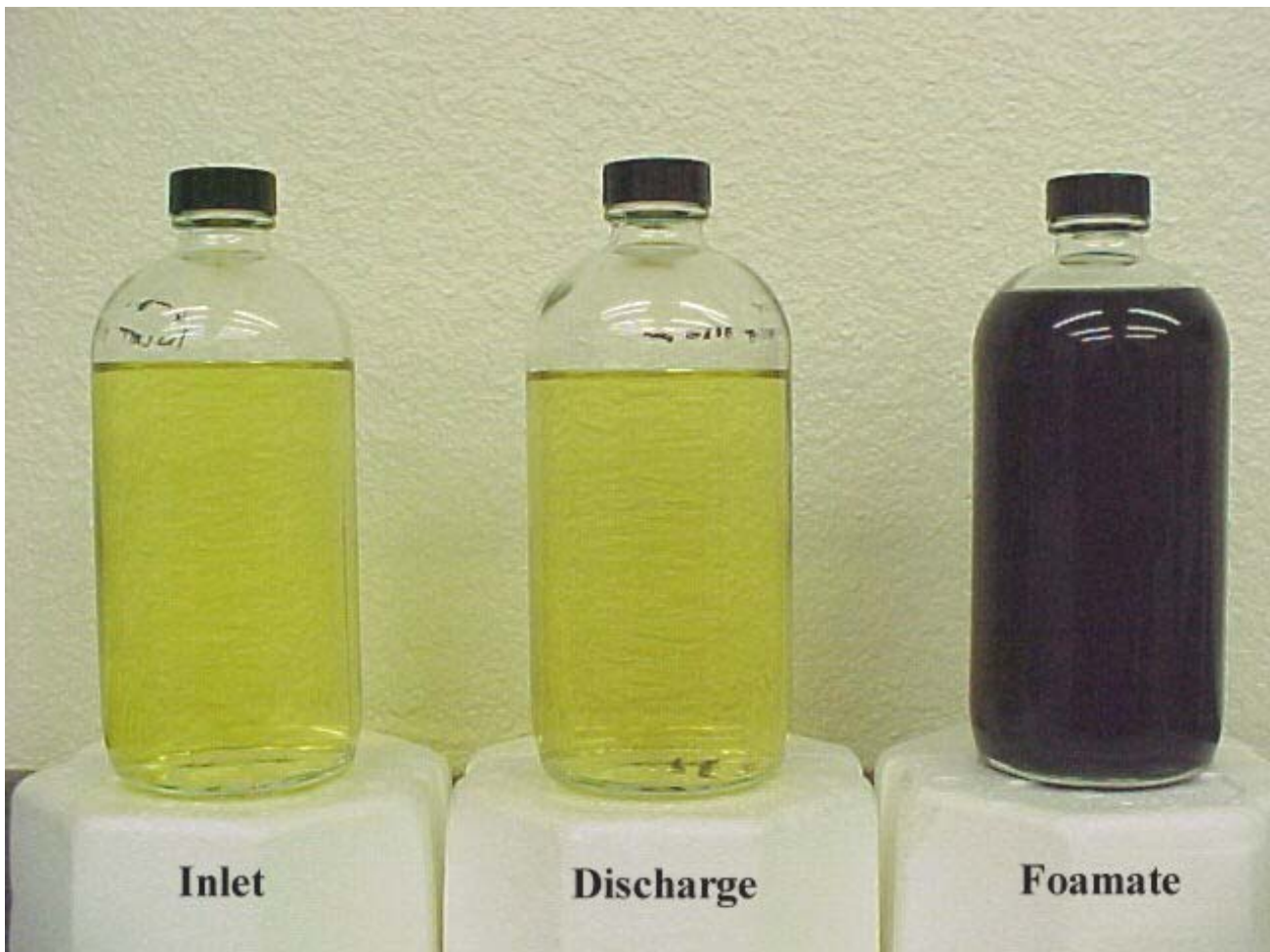
## CASE 2.0

The central amine system in this plant was not experiencing foaming problems at the time of the trial. However, they had a history of mysterious periodic upsets and were anticipating one at any time. Analytical work before, during and after previous upsets had produced inconsistent results so it was decided to see if the SigmaPure System could stop the problem, and/or help identify the actual cause.

The SigmaPure System underwent the inspections and leak testing prior to start up. The SP unit was tied into the plant on the lean feed to one of the plant's several contactors.

About an hour after the unit was started up, samples of the inlet and treated discharge were

**Figure 5.0. Case 2 Inlet, Treated Discharge, Foamate**



taken. As can be seen in figure 5.0, there were almost no visual differences in the inlet and discharge samples. We were literally shocked when we took the foamate sample, on the right, at the end of the two day run. However, when the plant engineering supervisor showed us an identical carryover sample taken during a previous massive upset, we were reassured that the sample was representative.

## CASE 2 PHYSICAL ANALYSIS

We took the inlet and outlet samples to the plant's laboratory and ran a foaming tendency test to see if the unit were having an effect on the, apparently clean, solvent. The results are given in

**Table 4.0 Case 2 Physical Analysis**

Description	TSS mg/l	Surface Tension		Foaming Tendency/Breaktime	
		78 deg F	120 deg F	80 deg F	120 deg F
Inlet Day 1	27.30	56.6	54.1	40/2	50/3
Discharge Day 1	13.10	60.0	56.0	40/2	30/2
Inlet Day 2	14.1	58.7	56.4	40/2	30/2
Foamate	33.2	54.3	53.4	50/3	60/7

table 4.0 Case 2 Physical Analysis.

The amine was within the accepted “50ml/2sec” parameter for non-foaming amine. Lower temperature should have favored higher foaming tendency, and faster breaktime. This is because surface tensions and viscosities are lower at elevated temperatures. Lower viscosities generally cause faster foam drainage, therefore shorter breaktime. Breaktime is also somewhat dependent on gas diffusion rates, e.g., coarsening. However, it isn’t known at this time how much gas diffusion influences breaktime under gas processing conditions. The physical tests were run at operating temperature to more accurately reflect the SigmaPure System effluent, and its reaction in the plant. Surprisingly, the breaktimes were longer. The samples were all rerun in our laboratory to verify the field tests.

Lower surface tension indicates the presence of surfactant. The inlet day 1 sample and foamate showed the lowest surface tensions. They were also the only samples that increase foaming tendency and longer breaktimes at the higher temperature. The day 1 discharge and day 2 inlet samples should have had the lowest surfactant concentration of the four samples. Consequently they exhibited a reverse tendency at the higher temperature, e.g., lower foaming tendency and shorter breaktimes.

The final results showed two important facts. First, our procedure of running foaming tendency and breaktime testing at operating temperatures yields more accurate data than the common ambient temperature testing. Second, the SigmaPure System’s function isn’t foaming tendency or break time dependent. The data clearly showed that, when tested under operating temperature, the foaming tendency and break time were improved despite the solvent not having an official foaming tendency. This would also explain why foamate was produced in the SP unit’s stripping column, although it took longer to accumulate.

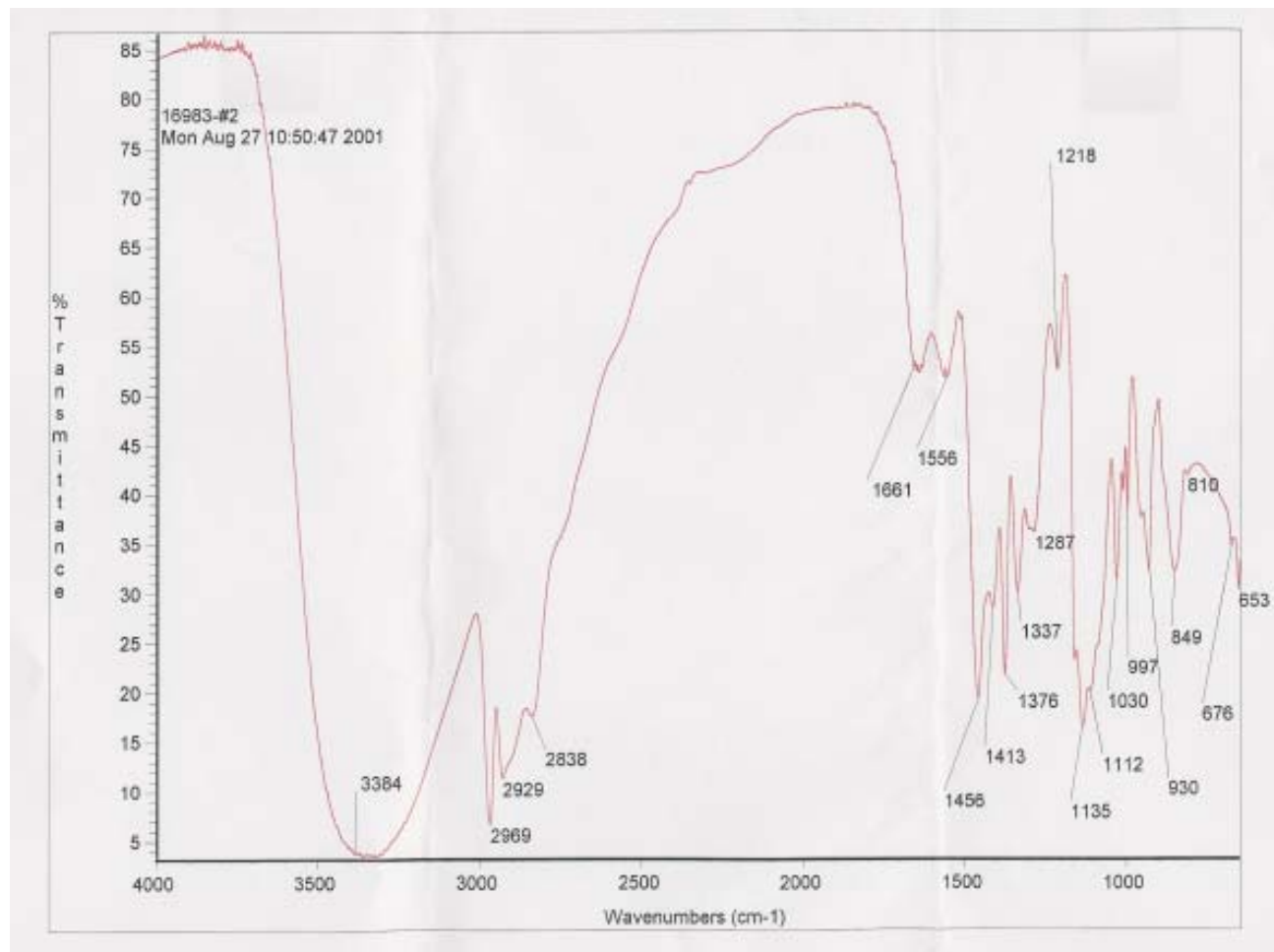
The total suspended solids data was consistent with previous laboratory and field trials with the unit. The SigmaPure System is quite effective at removing suspended solids because they are well known foam stabilizers. The solids removal wasn’t visually apparent until the foamate sample was taken because they were low initially low in concentration and generally below 1 micron in size.

## CASE 2 CHEMICAL ANALYSIS

Figure 7.0 is an FTIR scan of the foamate showing the functional groups of the contaminating compounds. These data were prepared as described in Case 1. The foamate was foamed again, collecting the foam, in the laboratory to further concentrate the foam causing contaminants. Table 7.0 shows the identification of each functional group shown on the scan.

Table 8.0 represents the scan data broken out in percent concentrations. Although not foaming enough to cause hydraulic problems in their towers, the surfactants present consisted of long chain carboxylic acids, sulfonates, ethoxylated alcohols, and glycols. We were also confident that, although the DIPA wasn’t causing a problem at that time, we were showing the contaminants that were causing their periodic problems. Further, we hadn’t seen long chain carboxylic acids in an amine sample before, so we suspected them to be one of the mysterious foaming culprits. We turned

**Figure 6.0 Case 2 FTIR Scan, Foamate**



**Table 5.0 Case 2 FTIR Scan Legend**

Wave Number	Characteristic Compounds
3384	Water, Hydroxides, Amines, Glycols
2969, 2979, 2838	CH <sub>2</sub> and CH <sub>3</sub> Aliphatic Hydrocarbon Chains
1661, 1556	Carboxylates (Fatty Acid Salts) and Amine Salts
1456, 1413	Aliphatic Hydrocarbons
1376	Aliphatic Hydrocarbons
1337	Amines
1287	Ethoxylated Alcohols (Non Ionic Detergents)
1218	Alkyl Sulfonates (Anionic Surfactants)
1160, 1135, 1112	Ethoxylated Alcohols (Non Ionic Detergents)
1303	Amines
930	Glycols
849	Glycols
810, 676, 653	Aliphatic Hydrocarbons

Total Organic Compounds - 66.8%

**Table 6.0 Case 2 Foamate Constituents**

Compounds	Concentration Percent of Total
Short Chain Carboxylic Acids	<1
Long Chain carboxylic Acids	20
Total Amines	40
Aldehydes	<1
Ketones	<1
Sulfonates	10
Ethoxylated Alcohols	20
Glycols	10

to our routine microscopic analysis for possible clues.

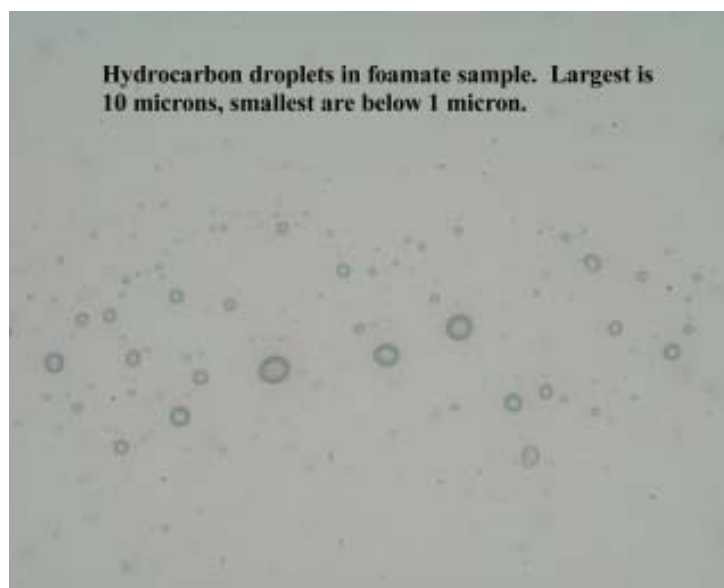
### **CASE 2 MICROSCOPIC ANALYSIS**

Case 2 photographs 1 and 2 represent the contaminants found in the foamate samples. Photo number 1 showed, what we believed to be, the source of the soluble long chain carboxylic acids in the foamate. These are microscopic droplets of entrained liquid hydrocarbon. By itself, the hydrocarbon wouldn't cause foaming. However, soluble fractions or soluble degradation products produced as the amine was stripped would account for the fatty acid surfactants.

Photo number 2 shows a common occurrence when immiscible liquids, i.e., liquid hydrocarbon or antifoam and solid particles, are present in amines; namely agglomerates. The small solids are wetted by the immiscible liquid and clump together. This is one of the causes of premature particle filter and activated carbon fouling.

Photo number 3 shows a sample of the "rag" layer of agglomerates removed from the process stream by the SigmaPure System. This sample was taken from the bulk gas - liquid interface in the

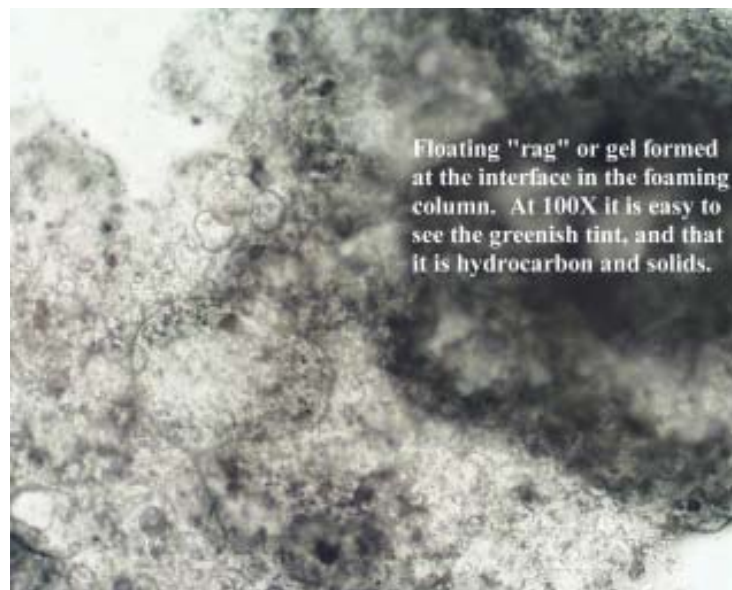
**Photo 1.0 Case 2  
Foamate**



**Photo 2.0 Case 2  
Foamate**



**Photo 3.0. Case 2  
Foaming Column  
“Rag” Layer**



SP unit's foaming column. We estimated that the rag layer was over an inch thick.

## **CASE 2 CONCLUSIONS**

Case 2 demonstrated that the SigmaPure System could be used to remove surfactants and foam stabilizing contaminants from “clean”, or non problem causing amine. There is no minimum foaming tendency or break time threshold for the SP system. Lower foaming properties simply translated into a longer period of time for foamate to appear. The surfactants scrubbed by the bubble cascade in the foaming column concentrated at the column's gas - liquid interface, as demonstrated by the presence of the rag layer. As the concentration of surfactants increased at the interface the break time also increased to the point where it would make the trip through the drying section to the stripping column. Therefore, even extremely low concentrations of surfactants in amine systems can be removed.

In addition to the foam causing surfactants, it was demonstrated that even extremely low concentrations of foam stabilizing solids and immiscible liquids below the 1 micron level were removed with the foam.

### CASE 3.0

This plant had a history of foaming upsets, and was being dosed with antifoam multiple times per day. The contaminants and source had not been positively identified, but solids carried into the plant with the feed were suspected as the main culprits.

The SigmaPure System was drawing lean solvent after the lean amine cooler and discharging into the absorber feed stream. The unit was brought on line after the normal inspections and leak testing. The start up was uneventful, however, within minutes a foam was visible in the foaming column sightglass. The liquid level was allowed to drop below the sightglass inlet to see the condition of the interface. Thick, high density foam was developing rapidly. The column's liquid level was allowed to increase to the normal operating position. After approximately 2.5 hours of operation the liquid level in the stripping column began to increase indicating the foam had already filled the drying section. This was the fastest response we had ever seen with the SP unit.

The plant operator came by after 18 hours of continuous operation and expressed surprise that they hadn't had to add antifoam on his shift. Approximately 3.2 gallons of foamate had been collected at that point. After 22 hours of operation, the sightglass began to become hazy. Within a few minutes the liquid level in the stripping column began to increase slowly. The level went up almost an inch in 30 minutes. At the same time the liquid in the sightglass became so foamy that the liquid level was difficult to detect. The plant's control room was contacted and confirmed that the absorber differential pressure was fluctuating and on the increase. It was decided to add antifoam,

**Figure 7.0 Case 3 Inlet, Treated Discharge, Foamate**



after which the differential pressure subsided. This cycle happened periodically throughout the run, although this was the only time antifoam was added to the system. We were able to predict even slight increases in tower differential pressure by watching the haziness of the SigmaPure System's foaming column sightglass.

The samples shown in figure 7.0, from left to right, are initial inlet, inlet after two days of treatment, and final foamate. The sampling strategy was to examine what was recirculating through the plant rather than what was being discharged from the SigmaPure System back into the plant. The color of the final inlet sample improved slightly. The optical clarity was significantly improved. There were no obvious suspended solids or immiscible liquids in any of the samples. As has come to be expected, the foamate sample was off color and very turbid. However, again there were no visible suspended solids or immiscible liquids.

### CASE 3 PHYSICAL ANALYSIS

The initial inlet sample showed a high concentration of suspended solids above 0.45 microns. This explained the sample's turbidity. The surface tension was considered to be high considering the amount of antifoam that had been added to the amine. The foaming tendency was low when the SigmaPure System's initial foaming response was taken into account. The explanation for the lower foaming tendency and the initial response by the SigmaPure unit turned out to be a function of amine viscosity. The SP unit was generating extremely small bubbles that produced very high density foam in the viscous amine. The sparger used in the laboratory produced bubbles that were much larger, consequently foam that was less dense. The larger bubbles produced lower density foam that drained, and subsequently broke more quickly than the foam being generated in the field unit.

The suspended solids were reduced quickly, dropping from 137.4 to 49.2 in less than 24 hours, and to 25.5 ppm by the end of the run.

**Table 7.0 Case 3 Physical Analysis**

Description	TSS	Surface Tension (100 deg F)	Foaming Tendency/Breaktime (100 deg F)	
	mg/l	dyne/cm	ml	seconds
7-26 Initial Inlet	137.40	44.5	60	3
7-29 Final Inlet	25.5	45.9	50	4
7-28 Final Foamate	47.2	40.9	320	45
7-27 Inlet During Upset	49.20	39.0	700	80
7-27 Inlet Sightglass Foam	145.2	46.6	ND	ND
7-29 Fomate Sightglass Foam	ND	39.4	ND	ND

The lower section of table 7.0 shows the physical results of a set of samples that were taken during the periodic "sightglass creaming" events. During one of these events, the inlet amine showed low solids content, but extremely low surface tension. The foaming tendency was quite literally almost more than could be measured. These data suggested that the solids present in the amine were not having a significant affect on the foaming tendency. They were incorporating in the foam, but probably weren't causing it.

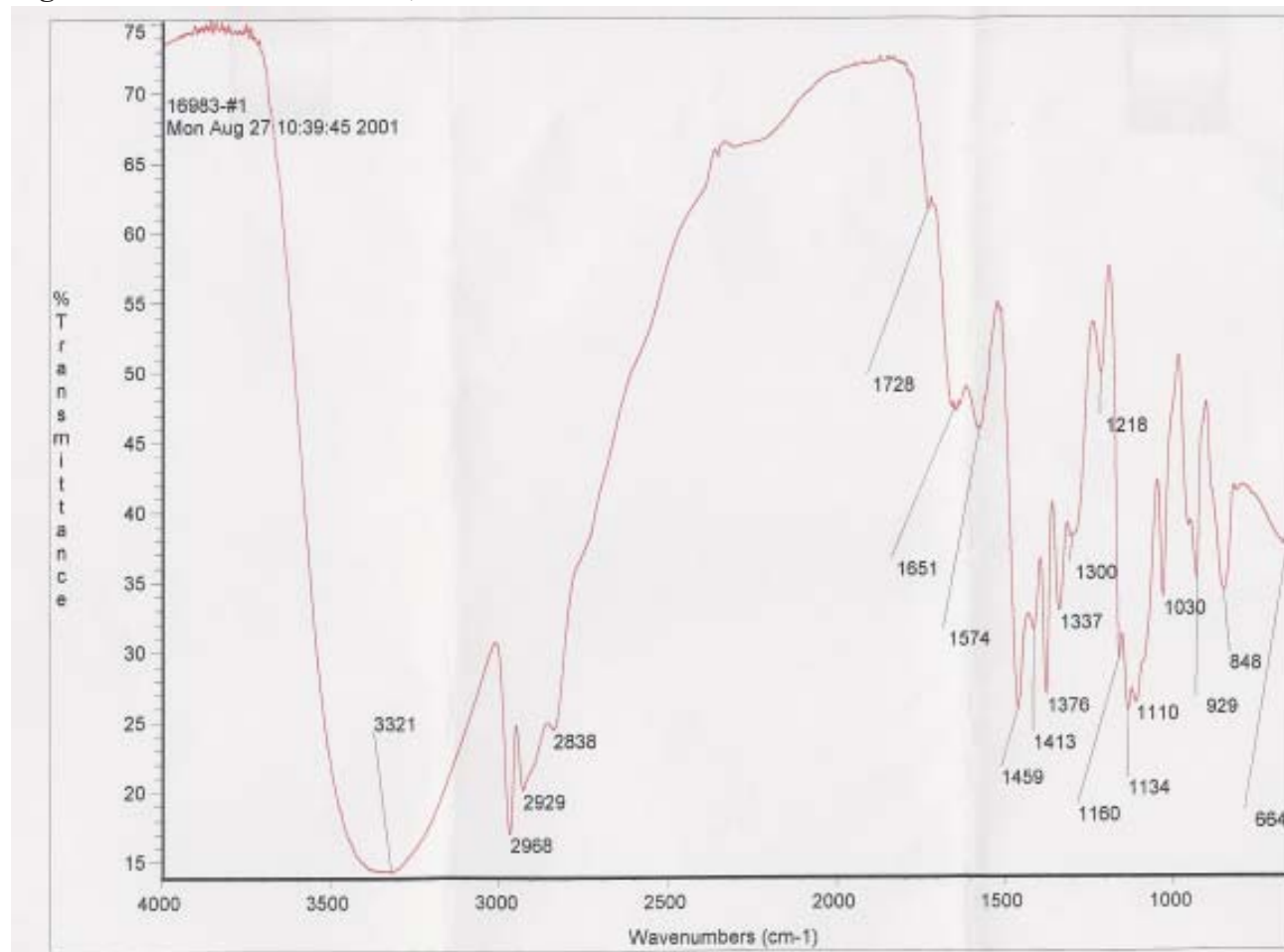
A sample of the pure foam from the foamate sightglass was taken. This sample represented the lowest surface tension of all of the samples. When compared with the inlet amine sample taken during one of the events, the surface tensions were almost indistinguishable.

### CASE 3 CHEMICAL ANALYSIS

Table 10.0 shows the FTIR scan of the concentrated foamate. Table 11.0 defines the functional groups of the compounds shown in the scan. Table 12.0 breaks out the scan data into percent concentration.

These data showed that long chain carboxylic acids were playing the largest foam development role. Sulfonates, ethoxylated alcohols and glycols were also involved as surfactants. It was not determined where the long chain fatty acids were originating. It was speculated that they were amine or, possibly even, antifoam degradation by products. However, to the best of the this author's knowledge, antifoam degradation has never been reported associated with use in sweetening plants.

Figure 8.0 Case 3 FTIR Scan, Foamate



**Table 8.0 Case 3 FTIR Scan Legend**

Wave Number	Characteristic Compounds
3321	Water, Hydroxides, Amines, Glycols
2968, 2929, 2838	CH <sub>2</sub> and CH <sub>3</sub> Aliphatic Hydrocarbon Chains
1728	Carboxylic Acids (Fatty Acids, Aldehydes, Ketones)
1651, 1574	Carboxylates (Fatty Acid Salts) and Amine Salts
1459, 1413	Aliphatic Hydrocarbons
1376	Aliphatic Hydrocarbons
1337	Amines
1300	Ethoxylated Alcohols (Non Ionic Detergents)
1218	Alkyl Sulfonates (Anionic Surfactants)
1160, 1134, 1110	Ethoxylated Alcohols (Non Ionic Detergents)
1030	Amines
929	Glycols
848	Glycols
664	Aliphatic Hydrocarbons

Total Organic Compounds - 64.8%

**Table 9.0 Case 3 Foamate Constituents**

Compounds	Concentration % of Total
Short Chain Carboxylic Acids	5
Long Chain Carboxylic Acids	20
Total Amines	35
Aldehydes	<1
Ketones	<1
Sulfonates	10
Ethoxylated Alcohols	15
Glycols	15

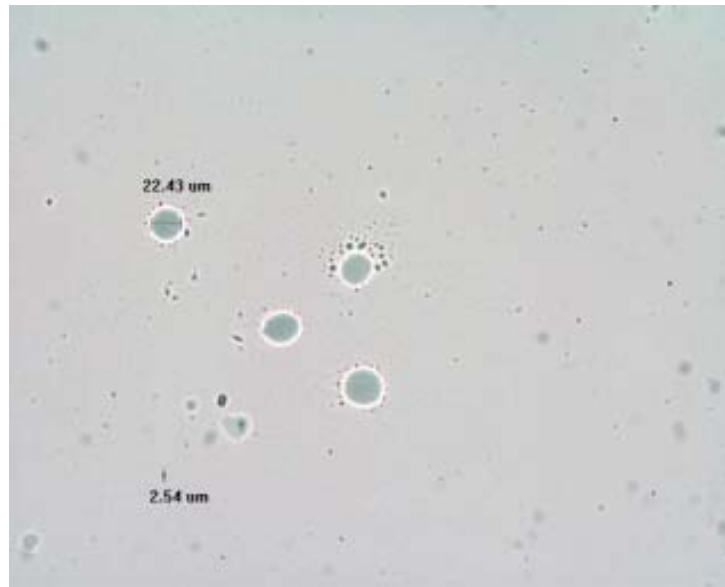
### CASE 3 MICROSCOPIC ANALYSIS

Photograph 4 shows immiscible liquid droplets seen in the initial inlet sample. It was known determined if these droplets were hydrocarbon or antifoam, but the latter is suspected since the plant was a tail gas treater.

Photograph 5 shows an agglomerate made up of immiscible liquid and wetted particles. Judging by the color the solids were most likely sulfur. The presence of agglomerates would explain why the surface tension was high in the samples that contained solids.

Photograph 6 a picture of a large agglomerate made up of antifoam and suspended solids. A large number of the solids seen in this sample were agglomerates.

**Photo 4.0 Case 3  
Initial Inlet**



**Photo 5.0 Case 3  
Initial Inlet**



**Photo 6.0 Case 3  
Initial Inlet**



### **CASE 3 CONCLUSIONS**

The SigmaPure System removed surfactant, solids, and immiscible liquid contaminants from the plant's amine. Operations added antifoam only twice while the SP unit was on line. However, the plant was seeing multiple contaminating events on an almost continuous basis so the foam causing contaminants were only being removed while the SP unit was running. Slightly over a week after the SP unit was disconnected the plant started to experience foaming problems again. The frequency of contaminating events could be seen by watching the SP units sightglass. It was obvious that this plant would require an SP unit on a continuous basis to stay out of trouble.

The surfactants causing the foaming problems were segregated and identified. Where the plant only suspected solids ingress as the problem, we were able to verify that solids were only part of a more complicated problem. The plant was definitely seeing surfactant ingress with the feed as well. Plant engineering immediately began to debate the possible sources.

A new, and potentially common surfactant was seen again; namely, long chain carboxylic acids. It was suspected that this surfactant was a liquid hydrocarbon or antifoam degradation product, but it's too early for a definitive conclusion.

#### **CASE 4.0**

This plant had a long history of sudden foaming upsets. The frequency and lack of effectiveness regardless of abatement efforts had caused the plant to use two different types of antifoam at the same time just to keep the plant operating.

The SigmaPure System underwent the typical inspections and leak testing prior to start-up. Feed was taken from the inlet side of the flash gas treater incorporated on the flash drum. The treated amine was discharged into the absorber feed.

Figure 5.0 shows the condition of the amine. The samples from left to right below represent the initial inlet, inlet after two days of operation, and final foamate. This case represents the first time the SigmaPure System effluent wasn't crystal clear, and is an example of a major advantage of

**Figure 9.0 Case 4 Inlet, Treated Discharge, Foamate**

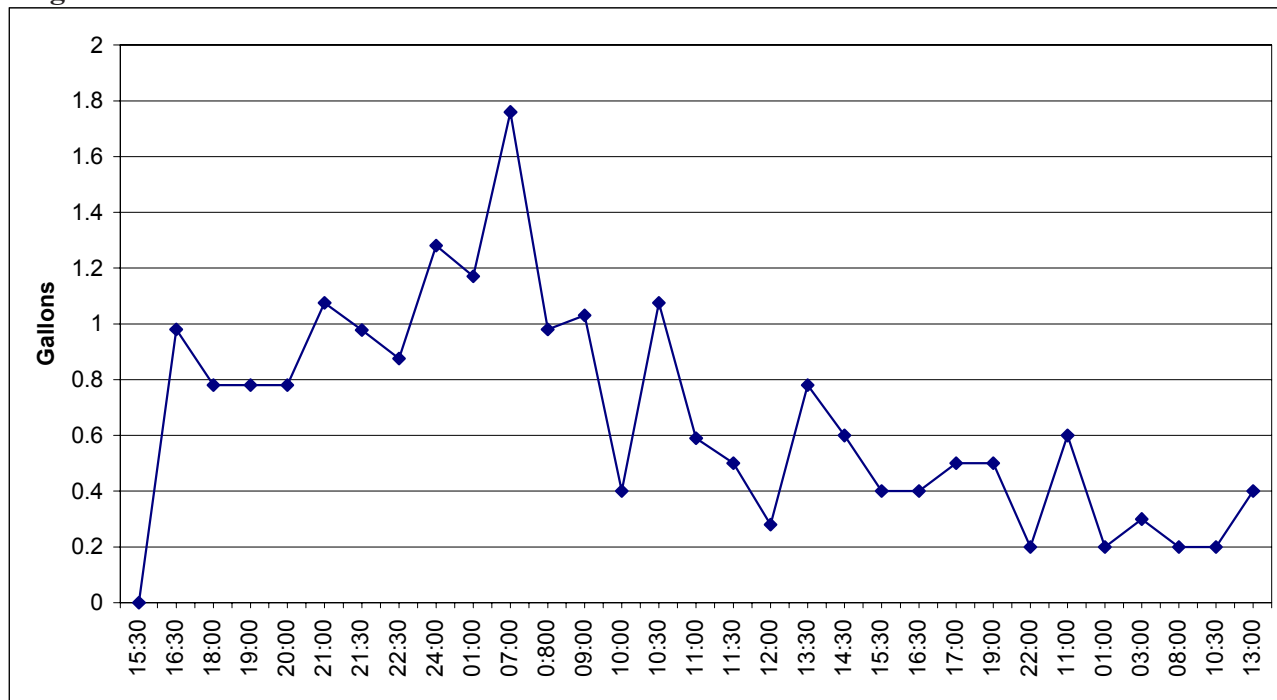


the system. The solvent components that were not responsible for foaming were not removed. We suspected the cloudiness was due to the antifoams injected into the system. Note the foam on the surface of the foamate sample. This picture was taken several hours after the samples were agitated.

#### **CASE 4 FOAMATE ACCUMULATION RATE**

Figure 10 shows the rates at which foamate was accumulated. The system was obviously cleaning up during the first 11 hours of treatment. The unit was isolated, but running in recirculation mode from 01:00 to 07:00. When flow was established at 08:00, the foamate collection rates trended

**Figure 10.0 Case 4 Foamate Accumulation Rate**



downward. At 32 hours of operation, the accumulation rate began to stabilize at 0.2 gallons per hour. This would be the profile of a plant that wasn't being contaminated on a continuous basis. The system was judged to be as clean as it was going to get without putting the SP unit in the plant on a long term basis. The foaming tendency and breaktime had been acceptable after 24 hours of operation.

**CASE 4 PHYSICAL ANALYSIS**

Table 10.0 shows the results of suspended solids, surface tension and foaming tendency testing. These data demonstrated a few reasons why examining amine samples through a microscope is critical to answering contamination questions. In previous trials solids had stabilized the foam, were consequently incorporated in the structure and removed. However, in this case there was less than 30% reduction in total suspended solids.

The initial inlet showed a considerable amount of suspended solids, and had a significant foaming tendency. The final inlet sample showed an increase in surface tension and below specification foaming tendency. The total suspended solids level had reduced somewhat, but nothing like previously seen through SigmaPure treatment. However, as previously stated, the unit would only remove those solvent constituents that cause or enhance foaming. The non-foam causing fractions were left alone.

The final foamate showed an incredible amount of solids and reduction of surface tension. The foaming tendency was so high it couldn't be determined quantitatively. Where did the solids in the foamate come from? There wasn't enough reduction in mass during the run to come close to a

**Table 10.0 Case 4 Physical Analysis**

Description	TSS mg/l	Surface Tension (140 deg F) dyne/cm	Foaming Tendency/Breaktime (140 deg F)	
			ml	seconds
Initial Inlet	173.06	36.7	150	60
Final Inlet	127.46	39.5	40	2
Final Foamate	261.86	34.8	>1000	>30 minutes

balance. The microscopic analysis showed the answer.

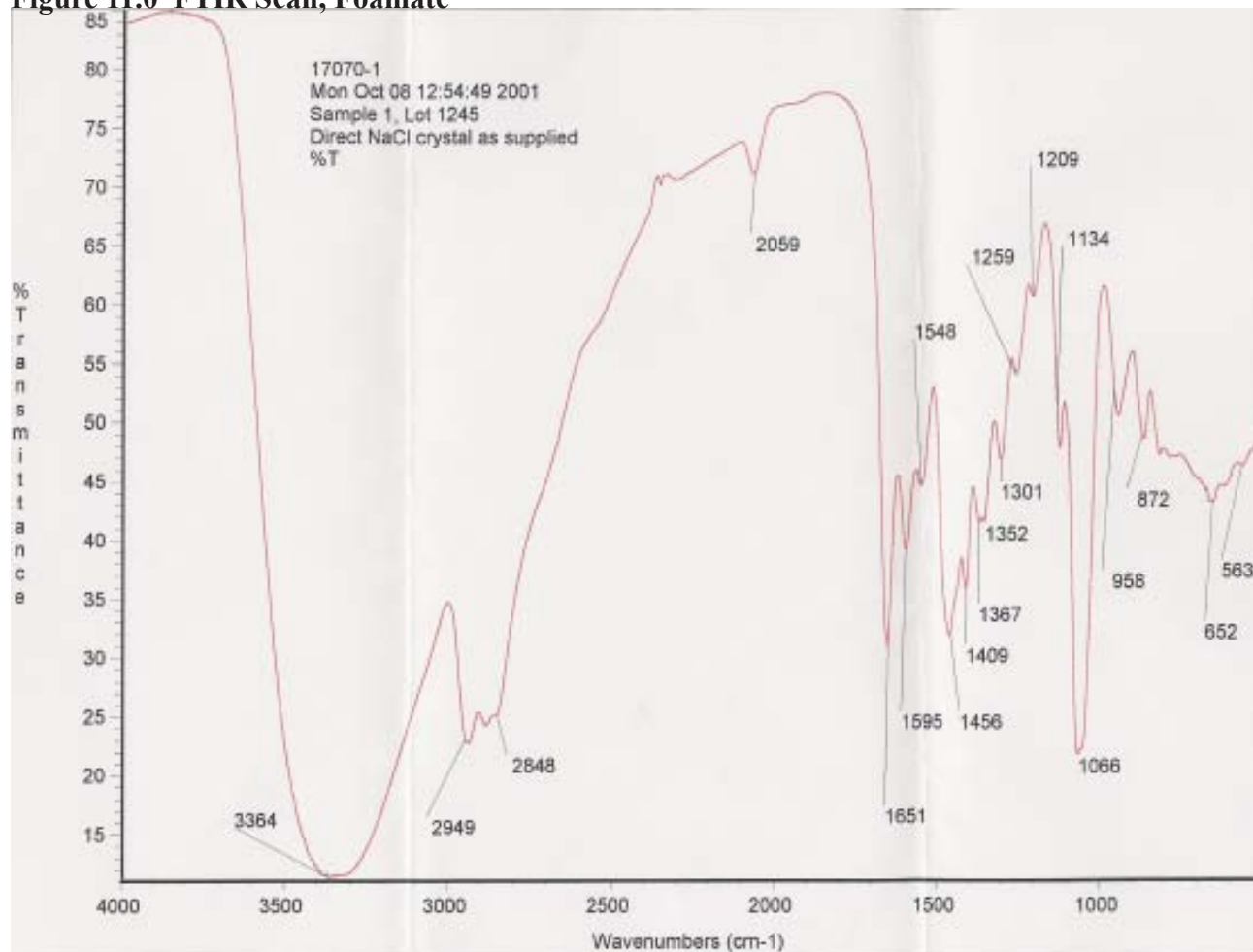
#### CASE 4 CHEMICAL ANALYSIS

Figure 11.0 shows the results of the FTIR analysis. Table 11.0 gives the identities of the peaks shown in the scan. Table 12 shows the data in percent composition.

Long chain carboxylic acids represented the highest concentration of all of the surfactants present in the amine. This system was known to see liquid hydrocarbon with the feed gas. As was seen in Case 2, where liquid hydrocarbon was a suspected contaminant and which also showed long chain carboxylic acids, these found in Case 4 could also be liquid hydrocarbon degradation related. However, these long chain fatty acids were also seen in Case 3 where the likelihood of finding hydrocarbon was low. The plant in Case 2 reported to add only small amounts of antifoam, where in Case 3 they added quite a bit. It should be noted that all three plants used alcohol based antifoam. We are not prepared to conclude that these large molecular weight fatty acids were coming from antifoam degradation, but it is highly suspect.

The other surfactants present included a small amount of sulfonates and glycols, with a significant amount of ethoxylated alcohols. It is known that one of the antifoams used in these system contained ethoxylated alcohols.

Figure 11.0 FTIR Scan, Foamate



**Table 11.0 Case 4 FTIR Scan Legend**

Wave Number	Characteristic Compounds
3364	Water, Hydroxides, Amines, Glycols
2949, 2848	CH <sub>2</sub> and CH <sub>3</sub> Aliphatic Hydrocarbon Chains
1651, 1595, 1548	Carboxylates (Fatty Acid Salts) and Amine Salts
1456, 1409	Aliphatic Hydrocarbons
1367	Aliphatic Hydrocarbons
1352	Amines
1301, 1259	Ethoxylated Alcohols (Non Ionic Detergents)
1209	Alkyl Sulfonates (Anionic Surfactants)
1134	Ethoxylated Alcohols (Non Ionic Detergents)
1066	Amines
958	Glycols
872	Glycols
652	Aliphatic Hydrocarbons

Total Organic Compounds - 31.9%

**Table 12.0 Case 4 Foamate Constituents**

Compounds	Concentration Percent of Total
Short Chain Carboxylic Acids	<1
Long Chain Carboxylic Acids	30
Total Amines	35
Aldehydes	<1
Ketones	<1
Sulfonates	5
Ethoxylated Alcohols	20
Glycols	10

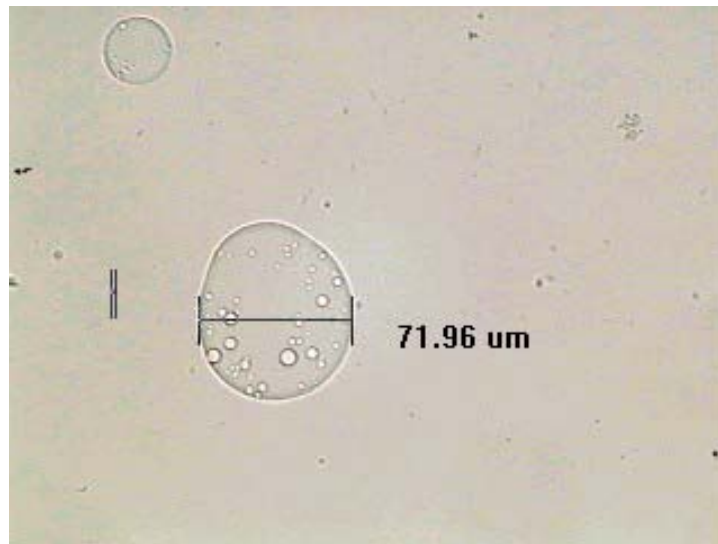
#### CASE 4 MICROSCOPIC ANALYSIS

Case 4 photographs 7-9 show some of the more unique contaminants found in these samples. Photo 7 is from the initial inlet, and shows two immiscible liquids with a surface affinity, but high enough surface energies that they didn't coalesce. It isn't known if these are two antifoam chemistries, or a hydrocarbon with an antifoam. The smallest particle shown in the photo is around 2 microns in diameter, and is a solid.

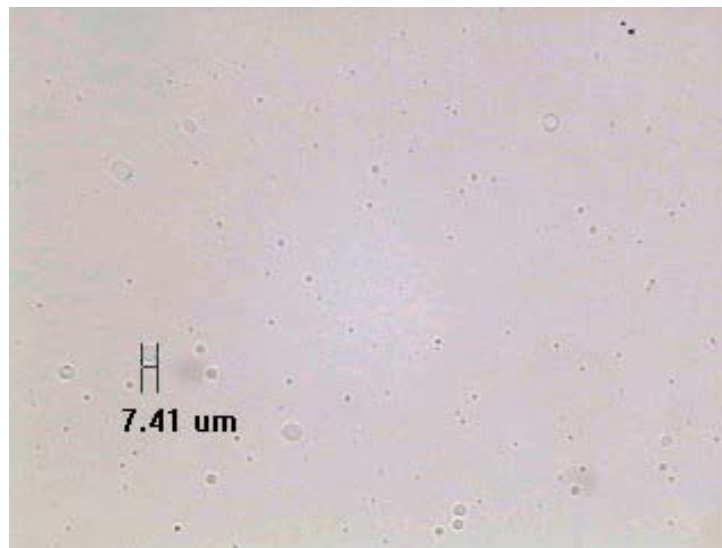
Photo 8 was taken from the final inlet. Considerable numbers of extremely small immiscible liquid droplets remained in the sample. These were suspected to be antifoam because the surface tension was not even above 40 dyne/cm. Note the lack of solid particles. Yet, the total suspended solids data reported over 120 ppm solids. If total suspended solids testing is done with 0.45 micron disks, per standard methods, they will likely be plugged with immiscible liquids if they are present. At least that is what we suspect happened in our tests. If the solids were there, we would have seen them under the microscope. Just as a side note, this is also why particle size distributions on amines with antifoam or hydrocarbon are almost meaningless. Modern particle counters cannot differentiate between solids and immiscible liquid droplets.

Photo 9 shows extremely emulsified immiscible liquid droplets, and larger solid particles seen in the final foamate. There were other examples of large bubbles of immiscible liquids as shown in photo 5.

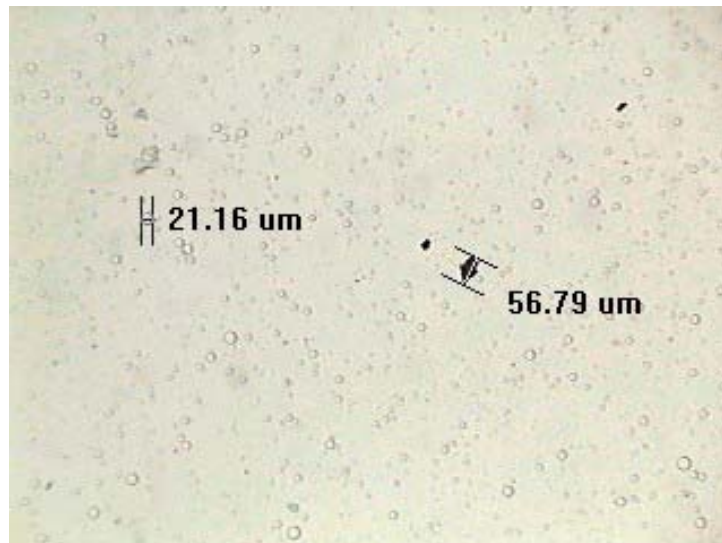
**Photo 7.0 Case 4  
Initial Inlet**



**Photo 8.0 Case 4  
Final Inlet**



**Photo 9.0 Case 4  
Final Foamate**



## CASE 4 CONCLUSIONS

It is a little early in the history of this technology to call any of its applications unique, but this case was unique. This was the first time we had worked with a system that used two different antifoams at the same time. Normal laboratory procedures would have determined that the suspended solids were exceptionally high. As a matter of fact, we didn't ask the question, but it's likely that the plant's particle filters are not showing much reduction in particle count or mass. The majority of the mass that was registering as total suspended solids was actually immiscible liquids. The only way to tell was microscopic analysis.

The operation of the SigmaPure System was exactly what we would expect from a plant that was severely contaminated by a single large event. It is interesting to note that the plant was not complaining of foaming while the unit was in operation. Foaming tests on the initial inlet samples showed it was foaming. The SP unit successfully removed the foam causing surfactants over the two day trial. The plant didn't upset and antifoam was not added to the system.

The final inlet sample remained turbid. This was another first for the SP System. It was an excellent example of how the unit removed only the contaminants that were responsible for foaming, while leaving all of the other solvent constituents alone. Related to the turbidity were large solid particles. There was no solvent pretreatment of any kind prior or during the SP unit's operation.

Once again, large molecular weight carboxylic acids were found to be among the surfactants present in the amine. The plant in Case 2 reported adding only small amounts of antifoam, and showed long chain fatty acids as well. There, we suspected a liquid hydrocarbon degradation by-product. In this case it could be either or both. These fatty acids will be a point of interest for us until we have the answer.

### **CASE 5.0**

This is another example of a fuel gas treater with a serious tendency for foaming upsets that were rated from bad to severe by plant personnel. As was the situation in Case 4, this plant was also treated with two different antifoams at the same time.

The SigmaPure System was piped up to take feed from the flash gas absorber, and discharge into the lean feed to the absorber. The unit was inspected and leak tested per prior to start up.

The samples taken are shown in figure 25 below, i.e., from left to right, initial inlet, final inlet, and final foamate. Although the photograph looks a little fuzzy, the initial inlet appeared fairly

**Figure 12.0 Case 5 Inlet, Treated Discharge, Foamate**

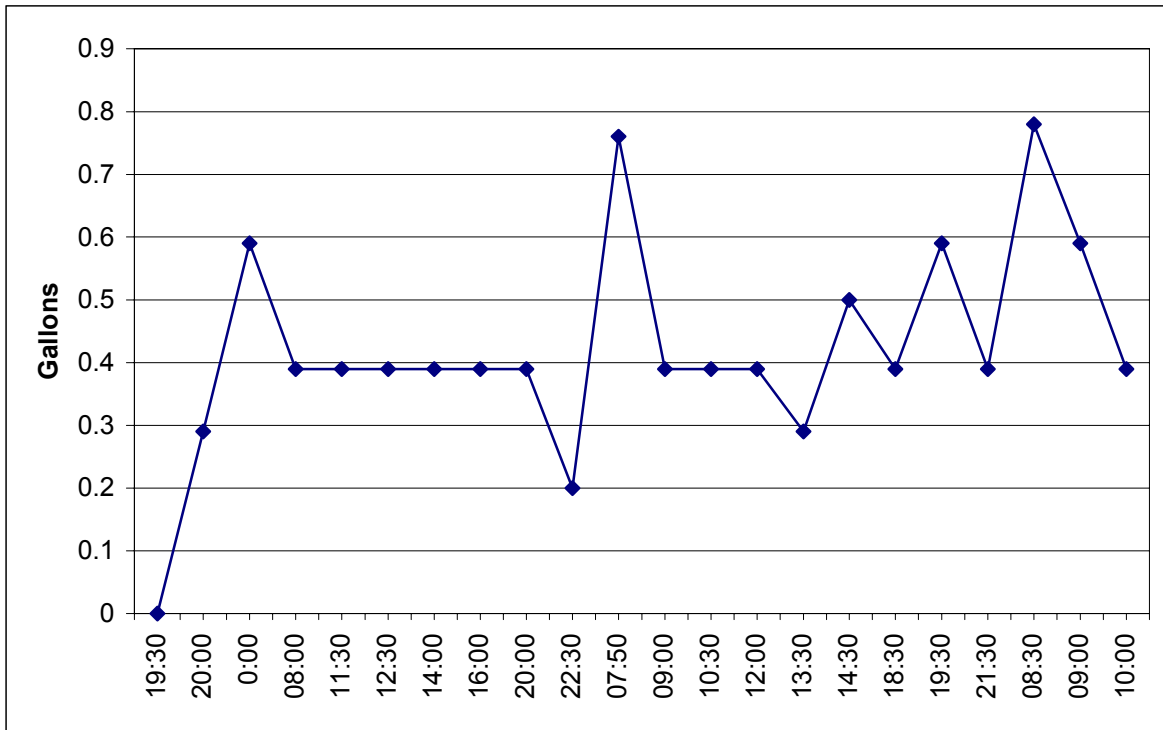


dark and turbid. The final inlet was much lighter amber with significantly improved clarity. The foamate was dark green, and very turbid. Note the foam on the surface of the foamate sample. The samples had been agitated about 3 hours before this photograph was taken.

### **CASE 5 FOAMATE ACCUMULATION RATE**

The graph in figure 26 shows the rate of foamate accumulation. As would be expected, the removal rate increased steadily from 19:30 to midnight. The SP unit collected about 0.3 gallons in the first 30 minutes of operation, and 0.6 for 4 hours thereafter. The removal levels fluctuated at about the same level until 13:30 the next day when the trend began to increase slightly. At that time,

**Figure 13.0 Case 5 Foamate Accumulation Rate**



one upstream feed sources was being starting up which caused incredible pressure swings throughout the plant. Despite the variances in pressure, it appeared as though the contaminant ingress to the plant was relatively constant.

**CASE 5 PHYSICAL ANALYSIS**

Examination of the data in table 13.0 shows the initial inlet with a total suspended solids level above 120 ppm. The surface tension was high at 46.5 dyne/cm, resulting in a foaming tendency and breaktime that was only slightly off spec (50ml/3sec). There was a significant increase in surface tension and subsequent reduction in foam height and breaktime with the final inlet sample. As expected, the total suspended solids concentration had been significantly reduced as well.

**Table 13.0 Case 5 Physical Analysis**

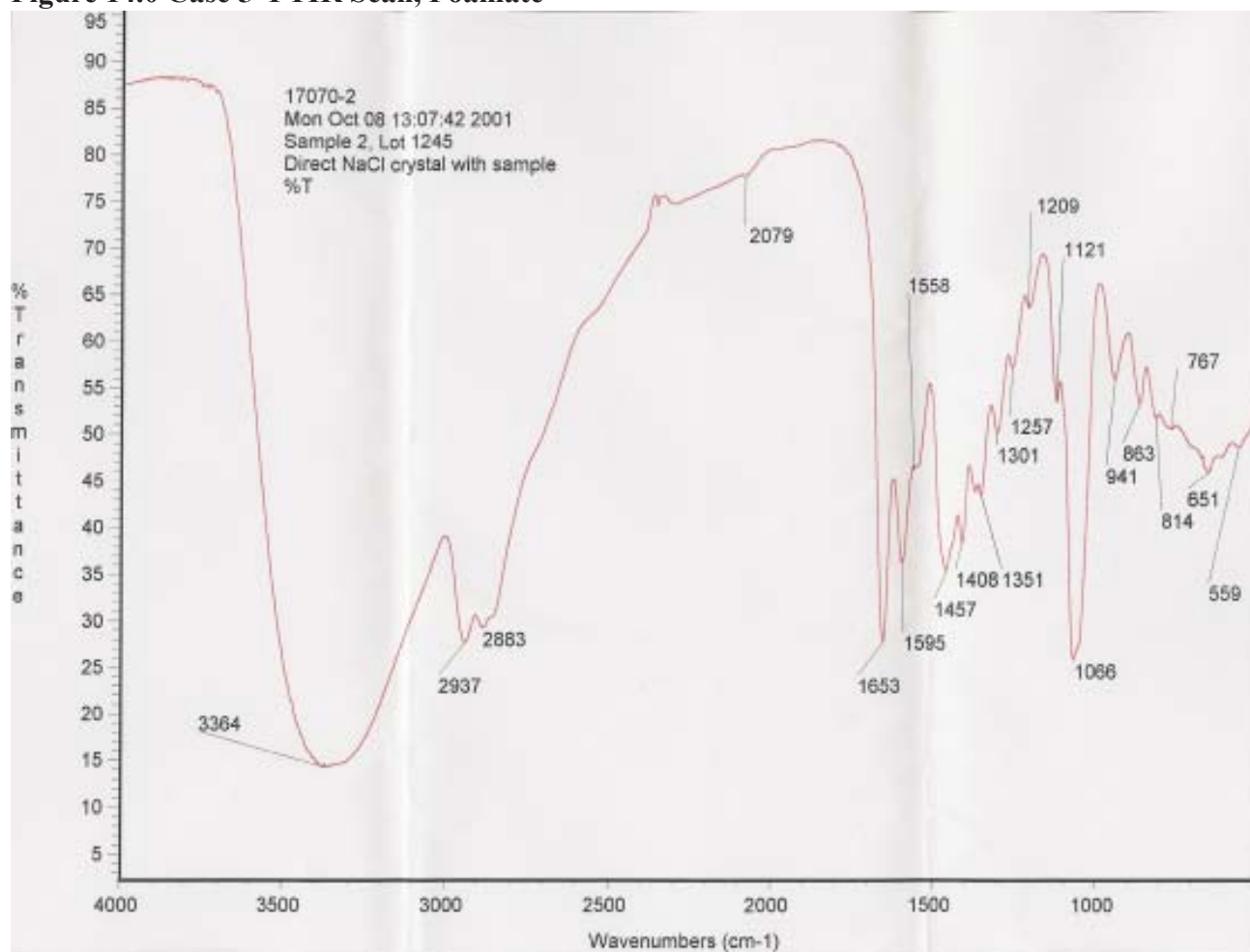
Description	TSS mg/l	Surface Tension (175 deg F) dyne/cm	Foaming Tendency/Breaktime (175 deg F)	
			ml	seconds
Initial Inlet	120.41	46.5	60	4
Final Inlet	79.38	49.4	40	2
Final Foamate	106.81	39.2	160	60

**CASE 5 CHEMICAL ANALYSIS**

Figure 14.0 shows the results of the FTIR scan on the foamate sample. Table 14 gives the definitions of the peaks in terms of functional groups. Table 15 shows the constituents in terms of percent composition.

The surfactants present in the foamate sample consisted of long chain carboxylic acids, a small amount of sulfonates and glycols, and ethoxylated alcohols. The ethoxylated alcohol based antifoam was used in this system, but not nearly to the extent as Case 4. Since this antifoam is being used, it cannot be concluded that the fatty acids are hydrocarbon degradation products.

**Figure 14.0 Case 5 FTIR Scan, Foamate**



**Table 14.0 Case 5 FTIR Scan Legend**

Wave Number	Characteristic Compounds
3364	Water, Hydroxides, Amines, Glycols
2937, 2883	CH <sub>2</sub> and CH <sub>3</sub> Aliphatic Hydrocarbon Chains
1653, 1595	Carboxylates (Fatty Acid Salts) and Amine Salts
1457, 1408	Aliphatic Hydrocarbons
1360	Aliphatic Hydrocarbons
1351	Amines
1301, 1257	Ethoxylated Alcohols (Non Ionic Detergents)
1209	Alkyl Sulfonates (Anionic Surfactants)
1121	Ethoxylated Alcohols (Non Ionic Detergents)
1066	Amines
941	Glycols
865	Glycols
814, 767, 651	Aliphatic Hydrocarbons

Total Organic Compounds -17.9%

**Table 15.0 Case 5 Foamate Constituents**

Compounds	Concentration Percent of Total
Short Chain Carboxylic Acids	<1
Long Chain Carboxylic Acids	30
Total Amines	35
Aldehydes	<1
Ketones	<1
Sulfonates	5
Ethoxylated Alcohols	20
Glycols	10

### **CASE 5 MICROSCOPIC ANALYSIS**

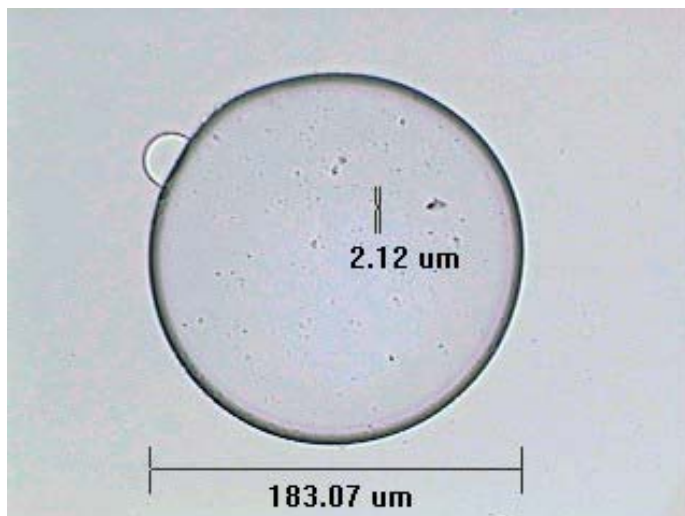
Photograph 10.0 is of the initial inlet. This is a shot of two immiscible liquid droplets of different substances. The larger droplet is covered with adsorbed solid particles in the 2.0 micron and smaller in size.

Photo 11.0 shows the extent of the solids contamination in the initial inlet. The solids shown were in the 1.0 to 20 micron range.

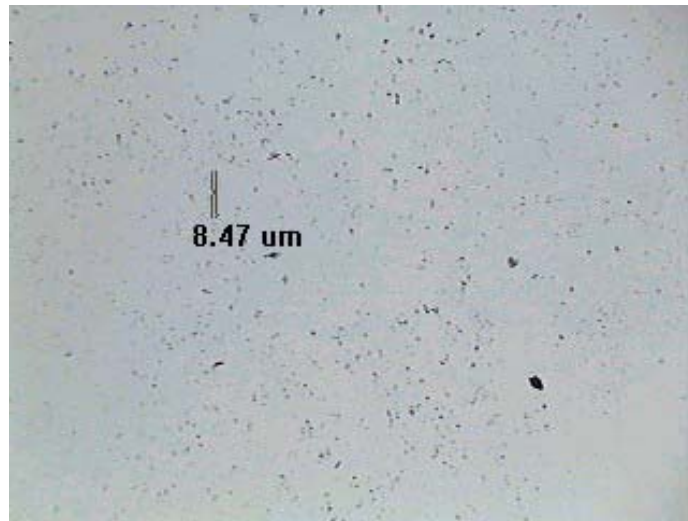
Photo 12 and 13 are of the final inlet shown is of the final inlet. These photos show the condition of the amine circulating in the process after SP treatment. The droplet shown is properly dosed antifoam that wasn't removed.

Photo 14 is of the foamate. This picture was included to show that even highly emulsified immiscible liquids are removed if they contribute to the foam development. These droplets are probably excess antifoam. The solids shown are well below 1.0 micron in size.

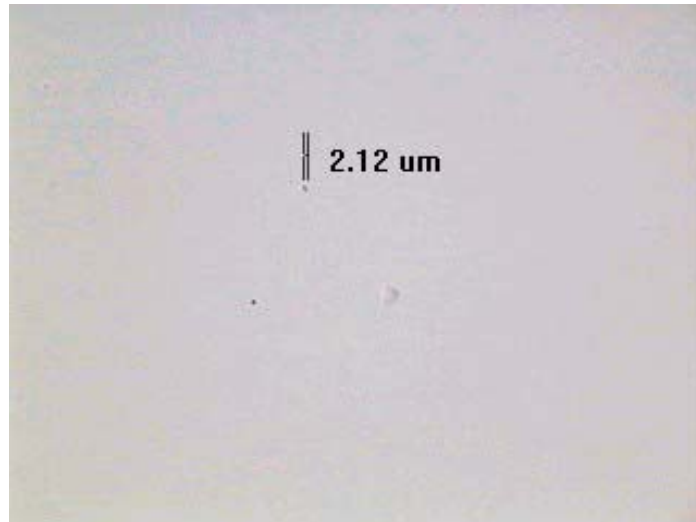
**Photo 10.0 Case 5  
Initial Inlet**



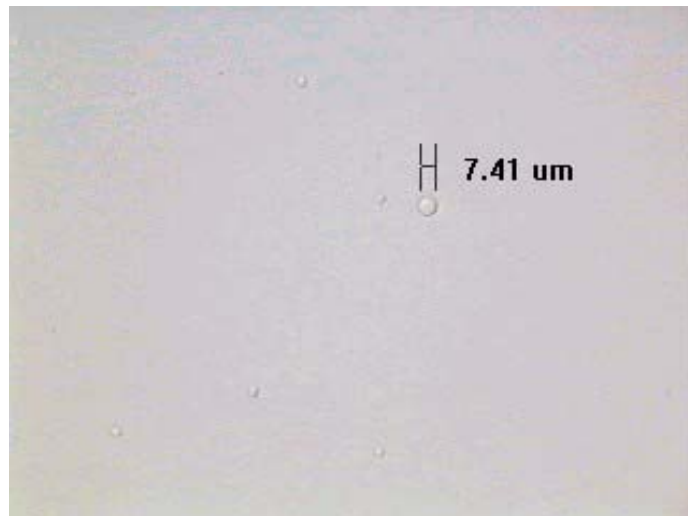
**Photo 11.0 Case 5  
Initial Inlet**



**Photo 12.0 Case 5  
Final Inlet**



**Photo 13.0 Case 5  
Final Inlet**



**Photo 14.0 Case 5  
Final Foamate**



### **CASE 5 CONCLUSIONS**

This plant was another with a long history of foaming upsets. According to plant personnel, this plant had occasional liquid hydrocarbon ingress. The initial inlet sample showed a relative high surface tension and subsequently low foaming tendency and breaktime. It wasn't reported to be foaming at the time of the trial. The suspended solids were high, but responded well to the SP unit treatment. The surface tension also increased with the removal of the surfactants in the amine.

An upstream gas source was being started up toward the end of the run, which caused pressure surges. The data showed an increase in surfactant removal during that time, indicating the surfactant might be latent in the piping, i.e., liquid hydrocarbon. The most concentrated surfactant found in the foamate were long chain carboxylic acids. However, this plant was using the same antifoam strategy as Case 4, so a definite conclusion can't be reached as to the source of the fatty acids.

The SigmaPure System operated without incident during the entire run. About midway through the trial the plant operator came out to ask what affect the treatment had on the amine activity. When it was explained that the unit only removed foam causing contaminants, the operator explained that the acid gas level in the treated gas had gone down while the SP unit was on-line. Improvements in gas to solvent mass transfer through surfactant removal will be the topic of a future SigmaPure paper.

## **INTRODUCTION QUESTIONS ADDRESSED**

### **Will the system actually work?**

The system actually works. Every plant in which it has been installed to date has responded in a measurable way. In each case, the frequency of antifoam addition was either reduced significantly, or eliminated completely. The towers responded with lower differential pressures when the solvents were foaming at the time of the trial. The unit produced measurable volumes, although small, of contaminating surfactants that were verified by physical and chemical tests. In a couple of the trials, the sources of contamination were verified so that abatement strategies could be formulated. In others, new and unique contaminants were identified which have warranted further study. And, in one application the efficiency with which the solvent removed acid gas was improved.

### **Is it solvent specific?**

As expected, the system doesn't appear to be solvent specific. However, we have found out that higher viscosity solvents have to be treated at higher temperatures. The adsorption bubbles produced by the system are so small that their settling time is affected. Slowing the settling time for the adsorption bubbles reduces the unit's treatment rate.

### **Does it have an affect on the solvent?**

There were no reports of negative affects with the surfactants were removed from the amines. There was one report of improved acid gas removal.

### **How long will the treatment last?**

We have found that the effectiveness of the treatment lasts until the plants recontaminate. In one case the system upset 30 hours after the unit was taken off line. In another the plant has not reported a foaming upset in over 6 months. We anticipated from the beginning that some plants would require a service and other a more permanent unit. That is specifically why we offer both.

### **What are the most common surfactants in amine systems?**

Frankly it's too soon to tell. This article contains examples of all of the surfactants we have identified thus far. We have predicted that, at the end of the day, the surfactants will be fractions from the contaminants already blamed for foaming, i.e., well treatment chemical, corrosion inhibitors, amine degradation products, liquid hydrocarbon, etc. To be honest, now that we have an indiscriminating method for their removal, the identification of the surfactant has almost purely academic. The most important reason for determining what they are is allowing the plants the opportunity to formulate abatement strategies.

### **Will the SigmaPure System eliminate the need for antifoam?**

We hope so, but sincerely doubt it. The fact is, if the ingress of surfactant becomes greater than the removal rate of the unit over a long period, the amines will produce foam. However, if the unit is on line, the foamate will be analyzed periodically to track the contaminant types and concentrations. Further, if there were a massive ingress to a clean system, the resulting upset would be far less intense than to a contaminated system that hadn't been treated.

Antifoam is a surfactant itself, and will be shown to inhibit mass transfer in these systems while it's masking surfactant contamination. There will be an occasional benefit for its use, with a more long term price to pay in efficiency.

## **ACKNOWLEDGMENTS**

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