Why Boilers Foam and How to Prevent It

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I.D. 1. INCH -STEAM OUTLER h- Zinch WINDOWS_ STAY BOLT -The state WATER I. COVERING GLASS WINDOWS WINDO 275 in. Pipe I.D. Zin. . 64 in: DIAM.

Background

In a steam boiler, salts present in the feedwater are concentrated as water is evaporated. This creates many challenges. Even if the most problematic salts, namely those that are responsible for scaling (calcium, magnesium, silicates, etc.), are well controlled and removed from the feed water by ion-exchange resins, reverse osmosis, or other methods, other ions may be present (sodium, potassium, chlorides, sulfates, and others) that will accumulate in the boiler and lead to foaming and carryover once certain critical concentrations are reached.

This fact limits the efficiency of the boilers, as a high proportion of the salt-laden water must be purged or "blown down" to reduce the concentration of these salts. This practice not only incurs energy costs, as the purged water is water that has been heated, but also costs of the supply, treatment and heating of the make-up water that must replace it.

Even though steam boilers are still, in many ways, at the heart of our industrial civilization, the phenomenon of foaming and carryover at high concentrations of salts has been subject to many misconceptions and erroneous explanations, such as "soapiness" due to high alkalinity or other surface-tension effects. This is not surprising, as the true explanation, presented here, is a water "anomaly" that involves the inhibition of bubble coalescence, which has been a subject of serious scientific study only since 1993.

Thus, organizations such as the American Society of Mechanical Engineers (ASME) or the American Boiler Manufacturer Association (ABMA) make recommendations as to the maximum conductivity allowed in boilers (a gross means of evaluating the salt concentration, without consideration of the types of ions involved) based on empirical historical observations, rather than on a scientific basis. Certain countries have even gone further than recommendations and enacted legislation to ensure that these limits are respected, again on purely empirical grounds.

The discovery of the relationship between bubble coalescence inhibition and foaming is explored in

this article to understand why tannin-based water treatment products can reduce or eliminate carryover in such circumstances. We will also explain why typical antifoam agents are not always useful and can often be detrimental when used to reach higher cycles of concentration. Finally, we will present a hypothesis as to how tannins function as antifoams and give examples of the gains in energy efficiency and greenhouse gas reduction that they can achieve.

Introduction

Foaming in boilers has been observed and has caused problems ever since boilers have been in use, that is, since the Industrial Revolution (1–5). The true physicochemical phenomenon that is its root cause is the inhibition of bubble coalescence at high concentrations of certain salts. Boaters who navigate both seas and freshwaters usually notice how much foamier the wake of their boats is in saltwater, but only in the first half of the 20th century was this phenomenon first studied. Unfortunately, these pioneering investigations were flawed in many ways (2-14). Inhibition of bubble coalescence was described more precisely in the 1960s and 1970s (15, 16) and more fully and fundamentally since the 1990s with competing theoretical explanations still being proposed to this day (17-49) and are even discussed on YouTube (youtu.be/mkBnZA8B_BM)!

Further studies have examined how this phenomenon affects the environment, for instance the oxygenation of the oceans (42) and the creation of small particles of seawater salts that serve as nuclei for the formation of rain clouds (50). The environmental impact of having small bubbles created in our ocean by wave action turns out to be of crucial importance to the biosphere. However, to date, the only envisaged potential application for industrial use has been for mining and mineral concentration processes that involve flotation (51–66) and desalination (67, 68). Its importance in steam production has been ignored even though preventing this phenomenon can greatly improve the efficiency of boilers.

Quite incredibly, the entire water treatment business for boilers as well as the steam equipment manufacturers have completely ignored these advances and still misunderstand why a boiler foams when the conductivity of the boiler water surpasses a certain level. Empirical guidelines have been established, for instance by the ASME and the ABMA, but one needs only peruse current boiler operator manuals, or course materials destined for power engineers, or various instructional websites of large water treatment companies, to discover that any explanation given to justify these is profoundly misguided and contrary to our recent scientific understanding.

Typically, the phenomenon is ascribed to high alkalinity or to the "soapiness" of highly alkaline solutions. It is also described as, or presumed to be, a foam accumulating at the surface of the boiler water. However, by verifying the surface tension values of solutions of salts that will accumulate as typical boiler waters are concentrated, one realizes that not only is there no decrease in surface tension (as a soap or surfactant would create), but, in fact, an increase. As well, observation of the bulk of the solution inside a foaming boiler clearly shows that the entire water mass is filled with small bubbles, rather than simply an accumulation of bubbles at the surface of the water, though both can certainly be seen under certain circumstances.

As mentioned, the first serious studies of foaming in boilers were done in the 1920s. For this purpose, C.W. Foulk of Ohio University constructed an experimental boiler with viewing ports (2) (Figure 1). He would spend 20 years elaborating a "Theory of Liquid Film Formation" (6) and would build various apparatus to explain his observations on bubbles and develop his theory (8). His early observations of bubbles in boilers were not precise, as he would alternate between descriptions of smaller bubbles being produced as salt concentrations increased (incorrect) and a transition from coalescing to non-coalescing bubbles that leads to smaller bubble size (correct). In 1931, he and his colleague Miller described and used a pumped air apparatus that he dubbed the *Dynamic Foam Meter* (7) that was to inspire quite a few similar devices used to study bubble coalescence, including our own muchimproved versions. Strangely enough, although Foulk's interest had started as an inquiry into foaming in boilers, he did not seem to have envisaged using his apparatus for practical purposes, such as optimizing boiler

performance or developing boiler antifoam formulations. This was to be done later, by scientists at the Dearborn Chemical Co. (now a part of Veolia).

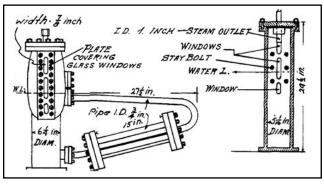


Figure 1: Foulk's experimental boiler with windows and his observations of the foamy mass of boiler water. From: Reference 5 (Foulk and Ryznar (1939).

There was a concerted effort in the 1940s and 1950s at Dearborn to develop antifoam chemicals. Long before any scientific study of foaming in boilers, many substances were recommended that were presumed to have an antifoam effect. Unfortunately, most of them, and notably the widely recommended Castor oil, would only work momentarily and after a short time would create a worsening of the foaming as they were degraded into surfactants. Two Dearborn scientists, Denman and Gunderson, discovered a variety of emulsified amines, fatty acid diamides, triamides, and others, which had the desired effect. Some had some commercial success, but unfortunately their properties waned quickly in boilers and were limited (69-90) in their applications. As we will see, most antifoams can be problematic.

These Dearborn scientists used tannins in their experiments as an adjuvant to create their dispersions of diamides and triamides and noted a clear synergistic effect as noted in the box under this paragraph (73). Unfortunately, they did not further explore the antifoam effects of tannins per se, even though tannin-treated boilers were historically known to foam much less. It is this effect of tannins, well-known to us and to all users of tannins, which motivated our work.

"It has been found that certain tannins are important synergistic substances that aid the polyamide compounds to 'cut in' effectively to inhibit foam formation, particularly in magnesium-containing and in 'low-solids' waters. The maintenance of higher alkalinity in such boiler water is also helpful."—From L. Gunderson and W. Denman, Reference 73.

Understandings (and Misunderstandings) of Carryover

Like most handbooks and courses for power engineers and other water-treatment specialists, we will delve into the reasons for carryover, but rather than divide the topic into three categories, which are namely: 1. "Priming"; 2. "Contamination"; and 3. "High conductivity/ High TDS (total dissolved solids)." We will replace the last one with "inhibition of bubble coalescence". As we will show, this will give us a better understanding of the true nature of this last type of carryover and will suggest avenues for surpassing traditional operating parameters.

Priming

Variations and especially sudden demands for steam leads to lower pressure, a rapid expansion of gases (Boyle's Law) and a surge of boiling. (Unbalanced boilers connected to the same header is also a common cause.) Keep in mind that expansion of gases is more rapid than a phase transition from water to steam, so that having a high percentage of steam in the boiler's water mass makes it more susceptible to priming. Also, sudden boiling depends on the presence of nucleation sites. However, as the rate of formation of vapor nuclei is proportional to e (Euler's number) to the power of $-\sigma^{3}$, where σ is the surface tension, any increase in the surface tension should be detrimental to a surge in boiling.

Moreover, as the force required to create a bubble in a liquid is proportional to $\sigma 3/2$, again, any increase in the surface tension should be detrimental to a surge in boiling (91). Knowing that an increase in TDS leads to an increase in surface tension in typical boiler water. This raises the question: Why should this lead to more susceptibility to priming rather than less, as physics would lead us to believe? As we will see, these

considerations are important in understanding how priming is linked to inhibition of bubble coalescence.

Contamination

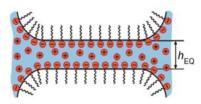
If surface-active substances enter the boiler, they will reduce the surface tension and create stable bubbles that accumulate and build up on the surface until they are sucked into the steam line. Very small amounts of surfactants are necessary. Also, as we've just seen, a decrease in surface tension should make the boilers more susceptible to surges of boiling, as there should be more nuclei and less pressure needed to create bubbles. Frequently, the contamination comes from vegetal or animal oils and greases that will be readily saponified in the high temperature and high pH of the boiler water. What is often not considered is that at high cycles and thus long residence times, most boiler polymers (including antifoams), will degrade, sometimes into small surface-active fragments. The physical phenomena are the same as those in a soap bubble, as illustrated in Figure 2.

Consequences of Small Bubble Sizes

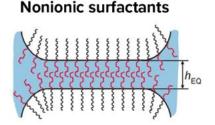
Explanations of why high TDS leads to carryover are found throughout the technical literature and abound with nonsense and contradictions. As we keep emphasizing, contrary to surfactants, the accumulation of salts typically found in boilers leads to an increase, not a decrease, in surface tension. Inhibition of bubble coalescence is a better way to describe this type of carryover, especially as high TDS does not necessarily lead to carryover.

Among the many scientific articles that have explored the subject (17-49), the one that first established this was Craig *et al.*'s 1993 article (18). He discovered that not all

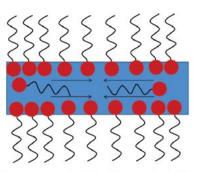
Ionic surfactants



Electrostatic stabilization



Steric stabilization



Marangoni effect repairs film

Figure 2: Stabilization of bubbles by surfactants. Images from Wikipedia.

ion pairs will lead to inhibition of coalescence, as seen in Figure 4. Based on experiments, he could classify each cation or anion as being an α (alpha) or a β (beta) type. Similar pairs, $\alpha\alpha$ and $\beta\beta$, will lead to inhibition as they are concentrated, but an $\alpha\beta$ pair or an $\beta\alpha$ can be concentrated without ever causing inhibition! For instance, a highly concentrated (high TDS), highly conductive solution of sodium acetate will *not* inhibit bubble coalescence, whereas a solution of NaCl will. This is illustrated in Video 1. Figure 3 shows a screenshot of the inhibition of bubble coalescence as shown in the video. The weblink to the video is given in the figure caption. Many theories have been proposed to explain this, but none are unanimously considered to be valid and to agree completely with the data. Developing a model has been a challenge for many reasons. Firstly, because it took some time to agree on how to measure the "Critical Coalescence Concentration" (CCC), which is a transition rather than a precise value, in view of the various methods and apparatus used. (Shown in Figure 4, right, and Figure 5.) Secondly, because combinations of α and β ions pose extra difficulties. Luckily, regarding α ions, the most commonly found in boilers, experiments have shown that the phenomenon can be understood

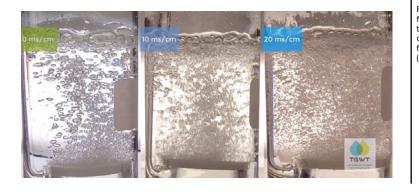


Figure 3: Screenshot from Video 1 that shows the inhibition of bubble coalescence as a function of conductivity (youtu.be/eahLMMVbFyM). best not in terms of concentrations or conductivities, but in terms of ionic strength, as seen in Figure 6 which shows data from a more precise measurement of bubble sizes by an image analysis technique.

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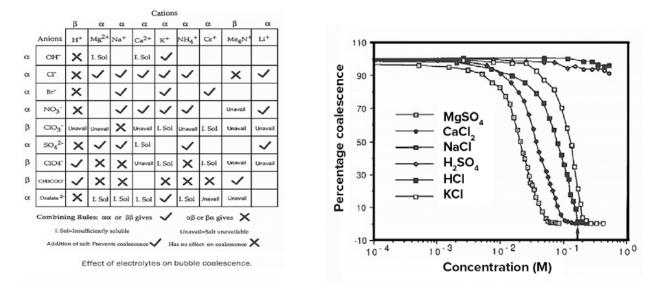


Figure 4: Only certain ion pairs will lead to inhibition of coalescence. Different salts have different "critical" concentrations at which this occurs, with doubly charged ions showing a lower concentration. From: (Craig, V., et al.), Reference 18.

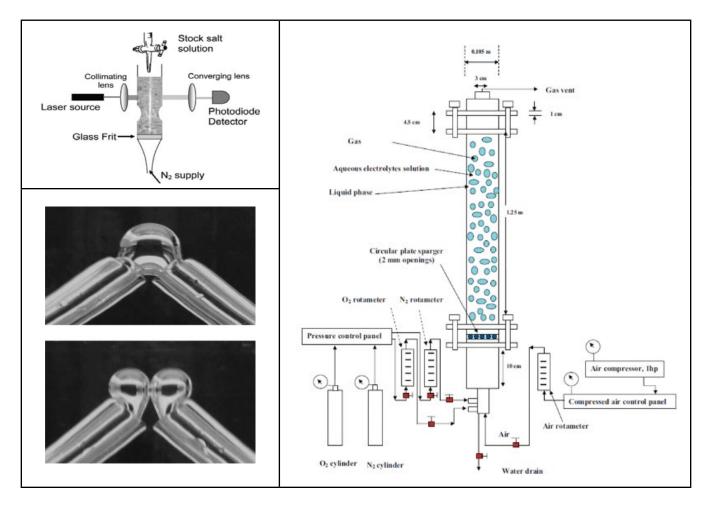


Figure 5: Various means of measuring the CCC of solutes include Turbidimetry, microscopic observations of pairs of bubbles, and gas holdup. One companyA has developed its own instruments (patent pending) to better simulate boiler conditions, using boiling water and steam rather than air or gas bubbles, production of uniform bubbles at a hot metal surface and detection of bubble size by three different means. The far-left image in Figure 6 is based on Reference 28 (Henry, et al.); the middle image is based on Reference 31 (Christenson, et al.), while the right image is from Reference 46 (Sujan and Raj).

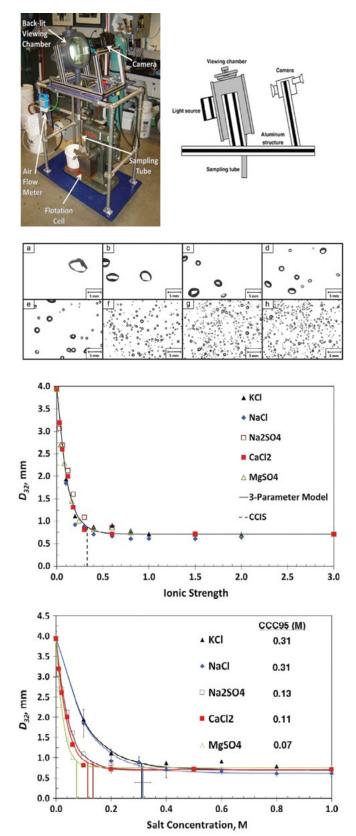


Figure 6: Top right: The McGill University bubble sampler apparatus designed to photograph bubbly water samples with bubbles in a single plane of focus. Top left: Such images allow for image analysis and determination of bubble size distributions. Bottom left: The CCC varies greatly according to the salt used. Bottom right: A model can be accurately fitted if the ionic strength of each salt is used instead of its concentration. Moreover, this model will work with mixtures of salts, as long as they are all of the a type. Top images from Reference 45 (Sovechles and Waters); bottom images from Reference 40 (Quinn, et al.).

Now that we have a better idea as to how inhibition of bubble coalescence occurs, we must see what the consequences of small bubbles in a boiler are. The first consequence is that the rising speed of the bubble will be reduced. (See Video 2, Figure 7.) An approximation would be the terminal speed of a spherical bubble, which is proportional to the square of its radius. This is illustrated in Equation 1:

Eq. 1

Where:

g is the gravitational acceleration (m/s₂) R is the radius of the spherical particle (m) ρ is the difference in density between the gas and the liquid (kg/m₃) μ is the dynamic viscosity (kg/m*s) v is the velocity (m/s)

(N.B.— Notice that in high-pressure boilers the difference in density between the steam and the water is greatly reduced and thus, so is the rising speed. This may exacerbate the propensity to carryover, though the lower viscosity may compensate.)

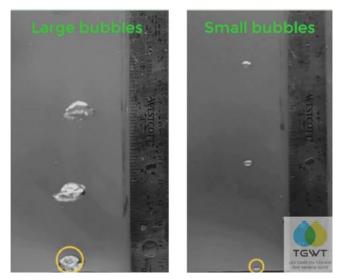


Figure 7: Video 2 screenshot: Speed of bubble rise in relation to bubble size (youtu.be/qyDuj7S6vx8).

Given a certain output of steam produced, a transition from large-to-small bubbles has a very deleterious effect. Many more and much smaller bubbles will be rising to the surface more slowly, so that a greater proportion of steam will be transiting through the boiler water, resulting in an increased gas holdup (Figure 9). This foamy mass will be more susceptible to rapid expansion with very small variations in pressure, thus making priming more likely. In addition, it will also give false level readings on sight glasses because the density of the foamy water is much lower than that of the bubble-free water in the sight glass.

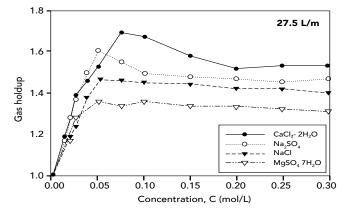


Figure 8: Gas holdup increases as various salts reach their CCC. The important changes (up to 70% for CaCl₂) vary also according to the rate of gas transiting through the water. Source: Reference 46 (Sujan and Vyas).

The second important consequence of having small bubbles is that these will eject droplets of boiler water as they burst at the surface. We know that the pressure differential between the inside and outside of a spherical bubble is inversely proportional to its radius as shown in Equation 2 (Laplace's Law):

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Pi–Po = 2σ/R
Eq. 2
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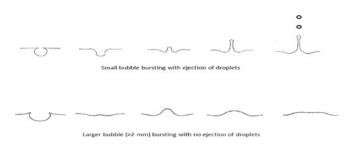
Where:

 σ is the surface tension (N/m)

P is the pressure (subscript *i* indicates inside, o is outside) (Pa or N/m^{2})

R is the radius (m)

Very small bubbles have extremely high pressures and will eject droplets when they burst. Then, as small droplets have a low terminal falling speed, it takes only a weak steam flow to carry them in the steam lines. (The same equation for the rising bubbles speed will apply for the terminal speed of a falling drop.) This was first seen in high-speed photography images taken decades ago (Figure 9). It can also be felt (and smelled, and tasted, and heard) when you are drinking a beverage with fine bubbles.



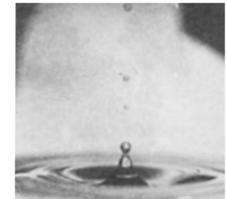


Figure 9: Top: The authors' rendering of the profile of a small versus a large bubble bursting. Bottom: High-speed photograph of a jet of small droplets being ejected from a small bubble bursting at the surface of water. Source: Kientzler, C. F., et al. (1954). "Photographic Investigation of the Projection of Droplets by Bubbles Bursting at a Water Surface," Tellus 6.1, pp. 1-7.

A third and final consequence of having small, slowly rising bubbles, is that for a given volume of steam their numbers will be extremely high. An example can illustrate this:

Let us assume that a 4-millimeter (mm) bubble is reduced to several 0.5-mm bubbles when inhibition occurs. We can easily calculate how many of smaller bubbles will hold the same quantity of steam. Since the volume is proportional to the cube of the radius, but the pressure inside bubbles increases inversely with the radius, you would need 64 of the smaller bubbles to contain the same amount of steam as in the large one. Of course, the distribution in bubble sizes is not narrow. As can be seen in our videos, a range of very small bubbles are formed. Because of their extremely slow rising speed, these will be caught in downward currents in the turbulent boiler water and will not easily reach the surface.

Their presence in large numbers has another extremely deleterious effect. They will act as the nucleation sites, or more precisely as precursors to larger bubbles that can easily form when a drop in the pressure of the boiler lowers the boiling point. The phase transition from water to steam will be greatly facilitated and carryover will ensue with much lower pressure drops. The phenomenon is analogous to the decompression of dissolved gases. If you shake a bottle to create swarms of bubbles, it will spurt when you open it, because you have more nucleation sites. (See Figure 10, which shows a screenshot from Video 3.)



Figure 10: Video 3 screenshot: The effect of increased nucleation sites due to inhibition of bubble coalescence (youtube.com/shorts/IcQWVMeXhbg).

To recap, inhibition of bubble coalescence in a boiler will occur when the total ionic strength of the boiler water reaches a critical value (the CCC) as long as the ions are of the α type (as most ions found in boilers are). At this point, the presence of small bubbles increases the likelihood of carryover through three paths:

- 1. An increase in the gas holdup volume due to the slow rise of bubbles.
- 2. A large number of salty boiler water droplets are being ejected by the bursting of small high-pressure bubbles.

3. Finally, the presence of a large number of small bubbles that can serve as nucleation sites when pressure drops occur.

It is worth mentioning that bubble coalescence does not only affect boiler performance in terms of carryover but may very well impact heat transfer across the boiler heating surfaces. As previously stated, steam bubbles will rise in boiler water until they attain a terminal velocity when the drag and buoyancy forces balance out. If the bubble size decreases due to the coalescence inhibition effect of ions present in the water, the drag force becomes dominant and the terminal velocity decreases. The drag force is further increased by the crowding effect of an increased number of smaller bubbles at the boiling surface. This leads to an increase in the residence time of bubbles near the metal surface and therefore a delay in their detachment and outflow into the bulk water, subsequently causing the vapor-generation rate to exceed the vapor-removal rate (92). Ultimately, this can create an insulating layer that can cause overheating of the metal surface, which could lead to disastrous consequences.

Strategies for Reaching High Cycles

Exceeding recommended limits can be extremely profitable and environmentally beneficial, but few dare to do so. When exploring this possibility, one should keep in mind that even the biggest players in the field of water treatment have put things in perspective regarding the ASME and ABMA recommendations:

"These guidelines should not be considered absolute. Some systems cannot tolerate operation at these concentrations; others operate continuously at significantly higher concentrations."

Source: Chapter 16 (Steam Purity) from the Veolia Water Technologies and Solutions' Handbook of Industrial Water Treatment. Accessible at www.watertechnologies.com/handbook/chapter-16-steam-purity.

Our improved understanding of the phenomena immediately suggests possible strategies:

Reduction of Ionic Strength

Reducing boiler chemicals that will add to ionic strength is a sure shot, but the gains are likely limited. We know that doubly or triply charged ions contribute much more to the ionic strength, because this varies with the square of the charge, as shown in Equation 3:

$$I = \frac{1}{2} \sum_{i=1}^{n} b_i z_i^2$$

Eq. 3

Where:

I is the ionic strength

b is the molality of ion i

z is its charge

Thus, we could increase our cycles by avoiding doubly charged ions such as sulfate (SO_4^2) - (the reaction product of sulfites) or phosphate (HPO_4^2) using different boiler chemistries that do not generate such ions.

Antifoams

Many antifoams will succeed in preventing the inhibition of coalescence, as seen in Figure 11. However, the most used boiler antifoam products, polyglycols and PGME (propylene oxide ethylene oxide polymer mono butyl ether), such as Dow's UCON[™], and hydrophobic silica particles in silicone oils, such as Dow's Xiameters[™], can only be used in low cycles or low-pressure boilers and with continuous feed. This is because, like the polyamides of the 1950s, they degrade readily at the high pH, temperature, and pressure of boiler water. At best, they lose their antifoam properties as the retention time increases with higher cycles, at worst, their degradation products are themselves surfactants that foam. (See Figure 12, and Figure 13 with screenshots from Videos 4 and 5.)

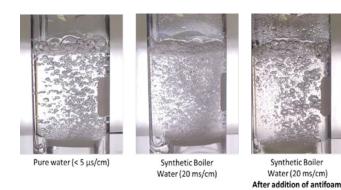


Figure 11: A silica/silicone oil antifoam prevents the inhibition of coalescence.

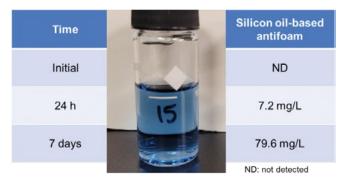


Figure 12: A sample of a silica/silicone oil antifoam has degraded into silicates (as indicated by the blue color, after exposure to boiler conditions, high pH, temperature, and pressure. Needless to say, the antifoam no longer functions.





CONTROL: Synthetic Boiler Water + Tannin Product after 120h at 180°C

Synthetic Boiler Water + Tannin Product + Polyglycolbased Antifoam at 0.1% after 120h at 180°C

Figure 13: Screenshots from Videos 4 and 5 that show the effect of antifoam degradation on boiler water foaming (Control: Video 4: youtube.com/shorts/ GZ1aI5ACeYM) and Video 5: (Experiment: youtube.com/shorts/7VITeCGUp_w).

Use of Tannins and Their Mode of Action

The starting point of our investigation into carryover was an attempt to understand why tannins have an antifoam effect. This has been observed time and again in systems that exceed the usual guidelines. (As well as in the lab, see Figure 14 that has a screenshot for Video 6.)

1. Pure Water	Carlos	Large bubbles no foaming
2. With salts 9000 mmhos		Simulating boiler water: Smaller bubbles & foaming
3. 9000 mmhos 1000 ppm of tannins		Back to larger bubbles & no foaming

Figure 14: Video 6 screenshot: The effect of tannins on bubble size. (youtu.be/kkNdixtk9to).

Effect of Tannins on Boiling Water and Carryover

Our understanding of inhibition of coalescence led us to explore two hypotheses:

- The tannate anion, like most organic anions, is probably a β-type anion, and its presence prevents the inhibition of coalescence due to the α-type cations and anions. This initially seemed the most plausible hypothesis, as tannins in solution exist as tannate ions that are more and more charged as the pH is increased. We cannot discount that this plays a role, but our experiments showed that it is not the primary mechanism.
- Tannins form particles of the right size and hydrophobicity to act as antifoam particles. We verified this in experiments in a small boiler (Figure 15.) that indicates that the antifoam action of tannins manifests itself clearly only in the presence of calcium (Ca²⁺) or magnesium (Mg²⁺) ions, with which they form complexes. (Figure 16). As pointed out previously, this had been noted for Mg²⁺ ions by Gunderson and Denman (73) in 1948.



Figure 15: This small electric boiler allowed us to perform simulations. Conditions: 125 to 150 pounds per square inch (psi) (353 to 366°F). Carryover simulations were done using NaCl/NaOH to reach the CCC at a threshold conductivity of 7,000 to 8,000 microsiemens per centimeter (μ s/cm) and physically by increase the steam demand. Tannins were effective at a level of 8 ppm in preventing carry-over at the moment of injection as well as after ~20 hours of operation, and beyond conductivities of 10,000 μ s/cm. Ca²⁺ ions were dosed using a solution of CaCl₂.

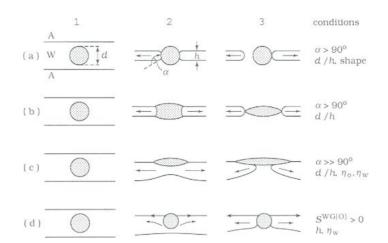


Figure 16: Possible mechanism of antifoam action of a soft solid calcium tannate particle illustrated in (a) or (d). Given the adequate size, as the solid particle finds itself in the liquid interface between two steam bubbles (Step 1), it will form a bridge between them (Step 2). At that point, due to its hydrophobicity, it will make the liquid de-wet the particle surface (Step 3) thus perforating the bubbles. Source: Bergeron, V.; Walstra, P. (2005). "7 – Foams," Fundamentals of Interface and Colloid Science, Lyklema, J., Academic Press. 5: 7.1-7.38.

Conclusion

Examples of Savings through High Cycles of Concentration with Tannin-Based Treatments

As always, shedding light on the physical and chemical processes in boilers opens avenues that can improve performance. We would therefore like to conclude with two case studies of savings achieved with higher cycles. These are a large pulp and paper mill (Figure 17) and a hospital (Figure 18), where we have tracked the savings accrued over the years, ever since a tannin treatment that allows for higher cycles began to be used. This enabled the end users to save on water (make-up and blowdown), energy (fuel costs), and reduce their carbon dioxide (CO_2) emissions, all the while continuing to protect their equipment.

For instance, over the course of almost 14 years of tannin treatment, the CHUS Fleurimont Hospital (in Sherbrooke, Quebec, Canada) was able to save a total of \$430,000 (all monetary figures in Canadian \$) while running at 100 to 150 cycles of concentration, and maintaining a condensate return conductivity of 10 to 20 μ s/cm. In another case study, the Cascades Cabano pulp and paper mill (in Témiscouata-sur-le-Lac, Quebec, Canada) implemented tannins for more than 11 years and realized \$2,760,00 in overall savings while running at 100 to 200 cycles of concentration and maintaining a condensate return conductivity of 5 to 10 μ s/cm.

	TOTAL SA	AVINGS (*based on a	an inflation rate of 2% p	per year)	
三三		1 year		11 years 2	months
⊢ (\$)		\$222,792		\$2,757,	261
		-	PWATER	SELVER	
GHG (CO2 E	EQUIVALENT)	MARE-U	PWATER	SEWER	WATER
1 year	11 years 2 months	1 year	11 years 2 months	1 year	11 years 2 months
699 t/year	7,806 t	24,015 m3/year	268,168 m3	27,214 m3/year	303,890 m3
\$20.00/t	\$24.87/t	\$1.00/m3	\$1.24/m3	\$1.00/m3	\$1.24/m3
\$13,981	\$173,028	\$24,013	\$297,184	\$27,211	\$336,762
SAME AS REMOVING FROM THE ROAD 152 MID-SIZE CARS	SAME AS REMOVING FROM THE ROAD 1,697 MID-SIZE CARS	SAME IN VOLUME AS 1,057 TANKER TRUCKS	SAME IN VOLUME AS 11,803 TANKER TRUCKS	SAME IN VOLUME AS 1,198 TANKER TRUCKS	SAME IN VOLUME AS 13,378 TANKER TRUCKS

 FUEL (SAVINGS PER YEAR)

 Oil nº6
 215,950 liter/year
 \$0.55/liter
 \$118,773

 Biomasse
 1,484 t/year
 \$23.00/t
 \$34,132

 SAME AS HEATING FOR 1 YEAR 729 RESIDENTIAL HOUSES (1500 SQUARE FEET)

Dil nº6	2,411,442 liter/year	\$0.68/liter	\$1,469,928
Biomasse	16,571 t/year	\$28.60/t	\$422,416

Figure 17: Savings in fuel, greenhouse gas emissions, make-up water and sewer water at a large pulp and paper mill.

	TOTAL SA	AVINGS (*based on a	an inflation rate of 2% p		
三月	8	1 year		13 years 7	months
= (\$)		\$27,898		\$430,6	04
CHG (CO2 6		Makeu	PWATER	SEWER	WATER
1 year	13 years 7 months	1 year	13 years 7 months	1 year	13 years 7 months
136	1,847	2,395	32,532	2,732	37,110
t/year	t	m3/year	m3	m3/year	m3
\$17.00/t	\$21.99/t	\$0.50/m3	\$0.65/m3	\$0.50/m3	\$0.65/m3
\$2,317	\$35,763	\$1,197	\$18,476	\$1,366	\$21,084
SAME AS REMOVING FROM THE ROAD 30 MID-SIZE CARS	SAME AS REMOVING FROM THE ROAD 407 MID-SIZE CARS	SAME IN VOLUME AS 105 TANKER TRUCKS	SAME IN VOLUME AS 1,426 TANKER TRUCKS	SAME IN VOLUME AS 120 TANKER TRUCKS	SAME IN VOLUME AS 1,630 TANKER TRUCKS

Natural gas	71,712 m3/year	\$0.30/m3	\$21,514
SAME AS HEATING F	OR 1 YEAR 57 RESIDENTIAL	OUSES (1500 SQUARE	FEET)
FUEL (SAVINGS	SINCE 13 years 7 months	:)	
FUEL (SAVINGS	SINCE 13 years 7 months 974,088 m3/year	s) \$0.39/m3	\$332.0

Figure 18: Savings in fuel, greenhouse gas emissions, make-up water and sewer water at a large university's teaching hospital.

These two examples along with many others illustrate how tannins can prevent carryover at higher boiler water conductivities. This research helped the authors understand the scientific complexities behind the bubble coalescence inhibition phenomenon while helping to show the antifoaming properties of tannins. δ_{-}

References

- Haswell, C.H. (1905). "Foaming of the Water in a Steam Boiler and Its Effect," *Scientific American* 92(5), p. 99.
- Foulk, C. (1924). "Foaming of Boiler Water," Industrial & Engineering Chemistry 16(11), pp. 1121-1125.
- Foulk, C.W.; Groves, K. (1933). "Foaming and Priming of Boiler Water," *Industrial* & Engineering Chemistry 25(7), pp. 800–803.
- Foulk, C. (1936). "Suspended Solids in the Foaming and Priming of Boiler Water," *Journal of the American Water Works* Association 28(4), pp. 528-536.
- Foulk, C.W.; Ryznar, J.W. (1939).
 "Foaming of Boiler Water," *Industrial & Engineering Chemistry 31(6)*, pp. 722-725.
- Foulk, C. (1929). "A Theory of Liquid Film Formation," Industrial & Engineering Chemistry 21(9), pp. 815-817.
- Foulk, C.W.; Miller, J. (1931). "Experimental Evidence in Support of the Balanced-Layer Theory of Liquid Film Formation," *Industrial & Engineering Chemistry* 23(11), pp. 1283-1288.
- Foulk, C.; Barkley, J.E. (1943). "Film Formation by Pure Liquids," *Industrial & Engineering Chemistry 35(9)*, pp. 1013-1016.
- Cassel, H.M. (1944). "Physical Aspects of Foaming in Steam Generation," Journal of Applied Physics 15(12), pp. 792-798.
- Schnurmann, R. (1929). "Die Grösse von Gasblasen in Flüssigkeiten (The Size of Bubbles in Liquids)," Zeitschrift für Physikalische Chemie (Journal of Physical Chemistry) 143(1), pp. 456-474.
- Schnurmann, R. (1937). "Über die Größe von Gasblasen in Flüssigkeiten (About the size of gas bubbles in liquids)," *Kolloid-Zeitschrift (Colloid Journal) 80(2)*, pp. 148-151.
- Schnurmann, R. (1939). "Antifoaming Devices," *Industrial & Engineering Chemistry 11(5)*, Analytical Edition, pp. 287-288.

- Schnurmann, R. (1939). "The Size of Gas Bubbles in Liquids and its Effects on the Rate of Dissolution of Metals in Liquids with Hydrogen Evolution and on Priming of Boiler Feed Water," *Journal of the Indian Chemical Society*, London, 58, p. 172.
- 14. Schnurmann, R. (1943). "On the Size of Gas Bubbles in Liquids," Navy Department, David W. Taylor Model Basin.
- Marrucci, G.; Nicodemo, L. (1967). "Coalescence of Gas Bubbles in Aqueous Solutions of Binorganic Electrolytes," *Chemical Engineering Science 22(9)*, pp. 1257-1265.
- Lessard, R.R.; Zieminski, S.A. (1971). "Bubble Coalescence and Gas Transfer in Aqueous Electrolytic Solutions," *Industrial & Engineering Chemistry Fundamentals* 10(2), pp. 260-269.
- Craig, V.S. Ninham, B.W.; Pashley, R.M. (1993). "The Effect of Electrolytes on Bubble Coalescence in Water," *The Journal of Physical Chemistry* 97(39), pp. 10192-10197.
- Craig, V.; Ninham, B.; Pashley, R. (1993). "Effect of Electrolytes on Bubble Coalescence," Nature, 364(6435), p. 317.
- Hofmeier, U.; Yaminsky, V.; Christenson, H. (1995). "Observations of Solute Effects on Bubble Formation," *Journal of Colloid and Interface Science 174(1)*, pp. 199-210.
- Christenson, H.; Yaminsky, V. (1995). "Solute Effects on Bubble Coalescence," The Journal of Physical Chemistry 99(25), pp. 10420-10420.
- 21. Craig, V.S. (2004). "Bubble Coalescence and Specific-Ion Effects," Current Opinion in Colloid & Interface Science 9(1-2), pp. 178-184.
- Marčelja, S. (2004). "Short-Range Forces in Surface and Bubble Interaction," Current Opinion in *Colloid & Interface Science 9(1-2)*, pp. 165-167.
- 23. Mucha, M.; et al. (2005). "Unified Molecular Picture of the Surfaces of Aqueous Acid, Base, and Salt Solutions," ACS Publications.
- Marcelja, S. (2006). "Selective Coalescence of Bubbles in Simple Electrolytes," The Journal of Physical Chemistry B 110(26), pp. 13062-13067.
- Jungwirth, P.; Tobias, D.J. (2006) "Specific Ion Effects at the Air/Water Interface," Chemical Reviews 106(4), pp. 1259-1281.
- Ribeiro, C.u.P.; Mewes, D. (2006). "On the Effect of Liquid Temperature Upon Bubble Coalescence," *Chemical Engineering Science 61(17)*, pp. 5704–5716.
- Ribeiro, C.u.P.; Mewes, D. (2007). "The Effect of Electrolytes on the Critical Velocity for Bubble Coalescence," *Chemical Engineering Journal 126(1)*, pp. 23-33.
- Henry, C.L.; et al. (2007). "Ion-Specific Coalescence of Bubbles in Mixed Electrolyte Solutions," *The Journal of Physical Chemistry C 111(2)*, p. 1015-1023.
- Ribeiro, C.u.P.c. (2008). "On the Estimation of the Regime Transition Point in Bubble Columns," *Chemical Engineering Journal 140(1)*, pp. 473-482.
- Karakashev, S.I.; et al. (2008). "Anomalous Ion Effects on Rupture and Lifetime of Aqueous Foam Films Formed from Monovalent Salt Solutions up to Saturation Concentration," *Langmuir 24(20)*, pp. 11587-11591.
- Christenson, H.; et al.(2008). "Electrolytes that Show a Transition to Bubble Coalescence Inhibition at High Concentrations," *The Journal of Physical Chemistry C 112(3)*, pp. 794-796.
- Craig, V.; Henry, C. (2010). "Inhibition of Bubble Coalescence by Salts and Sugars," Australian National University.
- Yaminsky, V.V.; et al. (2010). "Stability of Aqueous Films between Bubbles. Part 1: The Effect of Speed on Bubble Coalescence in Purified Water and Simple Electrolyte Solutions," Langmuir 26(11), pp. 8061-8074.
- Yaminsky, V.V.; et al. (2010). "Stability of Aqueous Films between Bubbles. Part 2: Effects of Trace Impurities and Evaporation," *Langmuir 26(11)*, pp. 8075-8080.
- Del Castillo, L.A.; Ohnishi, S.; Horn, R.G. (2011). "Inhibition of Bubble Coalescence: Effects of Salt Concentration and Speed of Approach," *Journal of Colloid and Interface Science 356(1)*, pp. 316-324.
- Nguyen, P.T.; et al. (2012). "The Influence of Gas Velocity, Salt Type and Concentration on Transition Concentration for Bubble Coalescence Inhibition and Gas Holdup," *Chemical Engineering Research and Design 90(1)*, pp. 33-39.
- Katsir, Y.; Marmur, A. (2014). "Rate of Bubble Coalescence Following Quasi-Static Approach: Screening and Neutralization of the Electric Double Layer," *Scientific Reports*, 4, p. 4266.
- Katsir, Y.; Marmur, A. (2014). "Rate of Bubble Coalescence Following Dynamic Approach: Collectivity-Induced Specificity of Ionic Effect," *Langmuir 30(46)*, pp. 13823-13830.

- Quinn, J. (2014). "Bubble Behaviour in Frother and Inorganic Salt Solutions," McGill University Libraries (Montreal).
- Quinn, J.; et al. (2014). "Critical Coalescence Concentration of Inorganic Salt Solutions," *Minerals Engineering*, 58, pp. 1–6.
- Firouzi, M. (2014). "Drainage and Stability of Foam Films during Bubble Coalescence in Aqueous Salt Solutions," The University of Queensland, School of Chemical Engineering.
- Katsir, Y.; Goldstein, G.; Marmur, M. (2015). "Bubble the Wave or Waive the Wubble: Why Seawater Waves Foam and Freshwater Waves Do Not?" *Colloids* and Interface Science Communications, 6, pp. 9-12.
- Firouzi, M.; Howes, T; Nguyen, A.V. (2015). "A Quantitative Review of the Transition Salt Concentration for Inhibiting Bubble Coalescence," *Advances in Colloid and Interface Science*, 222, pp. 305-318.
- Orvalho, S. (2015). "Bubble Coalescence: Effect of Bubble Approach Velocity and Liquid Viscosity," *Chemical Engineering Science*, 134, pp. 205-216.
- Sovechles, J.M.; Waters, K.E. (2015). "Effect of Ionic Strength on Bubble Coalescence in Inorganic Salt and Seawater Solutions," AIChE Journal 61(8), pp. 2489-2496.
- Sujan, A.; Vyas, R.K. (2018). "Estimation of Transition Concentration of Aqueous Mixtures of Single and Binary Electrolytes for Bubble Coalescence Inhibition," Chemical Papers, pp. 1-21.
- Dudek, M.; et al. (2019). "Microfluidic Method for Determining Drop-Drop Coalescence and Contact Times in Flow," *Colloids and Surfaces A: Physicochemical* and Engineering Aspects, p. 124265.
- Gong, S.; et al. (2019). "A Theoretical Model for Bubble Coalescence by Coupling Film Drainage with Approach Processes," *Chemical Engineering Science*.
- Duignan, T.T. (2021). "The Surface Sotential Explains Ion Specific Bubble Coalescence Inhibition," *Journal of Colloid and Interface Science*, 600, pp. 338-343.
- Blanchard, D.C.; Syzdek, L.D. (1988). "Film Drop Production as a Function of Bubble Size," *Journal of Geophysical Research: Oceans* 93(C4), pp. 3649-3654.
- Tavera, F.; Gomez, C.; Finch, J. (1996). "Novel Gas Hold-Up Probe and Application in Flotation Columns," *Transactions of the Institution of Mining and Metallurgy*. Section C. Mineral Processing and Extractive Metallurgy, 105.
- Tavera-Miranda, F.J. (1996). "Flow Cells to Measure Electrical Conductivity: Use in Estimating Gas Holdup in Flotation Systems," McGill University Libraries (Montreal).
- Tavera, F.; Gomez, C.; Finch, J. (1998). "Conductivity Flow Cells for Measurements on Dispersions," *Canadian Metallurgical Quarterly 37(1)*, pp. 19-25.
- Tavera, F.; Escudero, R. (2002). "Gas Hold-Up and Solids Hold-Up in Flotation Columns: On-Line Measurement Based on Electrical Conductivity," *Mineral Processing and Extractive Metallurgy 111(2)*, pp. 94-99.
- Gomez, C.; Finch, j. (2002). "Gas Dispersion Measurements in Flotation Machines," *CIM Bulletin 95(1066)*, pp. 73-78.
- Gomez, C.; Cortes-Lopez, F.; Finch, J. (2003). "Industrial Testing of a Gas Holdup Sensor for Flotation Systems," *Minerals Engineering 16(6)*, pp. 493-501.
- Gomez, C.O.; Finch, J.A. (2007). "Gas Dispersion Measurements in Flotation Cells,". *International Journal of Mineral Processing 84(1)*, pp. 51-58.
- Vinnett, L.; et al. (2018). "An Image Analysis Approach to Determine Average Bubble Sizes Using One-Dimensional Fourier Analysis," *Minerals Engineering*, 126, pp. 160-166.
- Hernandez Aguilar, J.R. (2004). "An Imaging Technique for Sizing Bubbles in Flotation Systems," McGill University Libraries (Montreal).
- Schwarz, S.; Alexander, D. (2006). "Gas Dispersion Measurements in Industrial Flotation Cells," *Minerals Engineering 19(6)*, pp. 554–560.
- Leiva, J.; et al. (2010). "Estimation of the Actual Bubble Surface Area Flux in Flotation,". *Minerals Engineering 23(11-13)*, pp. 888-894.
- Vinnett, L.; Contreras, F.; Yianatos, J. (2012). "Gas Dispersion Pattern in Mechanical Flotation Cells," *Minerals Engineering*, 26, pp. 80-85.
- Vinnett, L.; Alvarez-Silva, M. (2015). "Indirect Estimation of Bubble Size Using Visual Techniques and Superficial Gas Rate," *Minerals Engineering*, 81, pp. 5-9.
- 64. Vazirizadeh, A. (2015). "The Relationship Between Hydrodynamic Variables and Particle Size Distribution in Flotation," *Materials Science*.
- 65. Vazirizadeh, A.; Bouchard, J.; del Villar, R. (2015). "On the Relationship between Hydrodynamic Characteristics and the Kinetics of Column Flotation. Part I: Modeling the Gas Dispersion," *Minerals Engineering*, 74, pp. 207-215.

- Vazirizadeh, A.; Bouchard, J.; Chen, Y. (2016). "Effect of Particles on Bubble Size Distribution and Gas Hold-Up in Column Flotation," *International Journal of Mineral Processing*, 157, pp. 163-173.
- Francis, M.J.; Pashley, R.M. (2009). "Thermal Desalination Using a Non-Boiling Bubble Column," *Desalination and Water Treatment 12(1-3)*, pp. 155-161.
- Shahid, M.; Pashley, R.M. (2014). "A Study of the Bubble Column Evaporator Method for Thermal Desalination," *Desalination*, 351, pp. 236-242.
- Denman, W.L. (1942). "Method of Treating Waters, Including Boiler Waters and Compositions Therefor," U.S. Patent No. 2,304,805, United States Patent Office, Washington, D.C.
- Gunderson, L.O. (1943). "Method of Conditioning Water," U.S. Patent No. 2,328,551, U.S. Patent Office, Washington, D.C.
- Gunderson, L.O. (1945). "Method of Conditioning Water," U.S. Patent No. 2,366,727, U.S. Patent Office, Washington, D.C.
- Denman, W.L. (1946). "Method of Treating Waters, Including Boiler Waters, and Composition Therefor," U.S. Patent No. 2,410,543, U.S. Patent Office, Washington, D.C.
- Gunderson, L.; Denman, W. (1948). "Polyamide Foam Inhibitors," Industrial and Engineering Chemistry 40(8), pp. 1363-1370.
- Gunderson, L.O. (1948). "Method of Conditioning Water," U.S. Patent No. 2,442,768, U.S. Patent Office, Washington, D.C.
- Gunderson, L.O. (1949). "Method of Inhibiting Foaming in Steam Boilers," U.S. Patent No. 2,485,378, U.S. Patent Office, Washington, D.C.
- Gunderson, L.O. (1949). "Method of Inhibiting Foam Formation in an Aqueous Gas-Liquid System," U.S. Patent No. 2,461,730, U.S. Patent Office, Washington, D.C.
- Gunderson, L.O. (1950). "Amide Composition," U.S. Patent No. 2,528,274, U.S. Patent Office, Washington, D.C.
- Gunderson, L.O. (1950). "Method of and Composition for Inhibiting Foaming in Steam Boilers," U.S. Patent No. 2,485,378, U.S. Patent Office, Washington, D.C.
- Gunderson, L.O. (1950). "Prevention of Foaming in Steam Generation," U.S. Patent No. 2,493,453, U.S. Patent Office, Washington, D.C.
- Gunderson, L.O. (1950). "Method of Inhibiting Foaming in Steam Boilers," U.S. Patent No. 2,528,273, U.S. Patent Office, Washington, D.C.
- Gunderson, L.O. (1952). "Method and Composition for Inhibiting Foam in Aqueous Systems," U.S. Patent Office, Washington, D.C.
- Gunderson, L.O. (1952). "Prevention of Foaming in Steam Generation," U.S. Patent No. 2,600,361, U.S. Patent Office, Washington, D.C.
- Gunderson, L.O. (1952). "Prevention of Foaming in Steam Generation," U.S. Patent No. 2,583,771, U.S. Patent Office, Washington, D.C.
- Gunderson, L.O. (1952). "Method of Inhibiting Foam Formation in Steam Generation," U.S. Patent No. 2,596,925, U.S. Patent Office, Washington, D.C.
- Gunderson, L.O. (1952). "Acid and Quaternary Salts of Polyamides," U.S. Patent No. 2,583,772, U.S. Patent Office, Washington, D.C.
- Gunderson, L.O. (1953). "Compounds for Altering Surface Characteristics of Liquids," U.S. Patent No. 2,630,439, U.S. Patent Office, Washington, D.C.
- Gunderson, L.O. (1953). "Method of Inhibiting Foaming in Water," U.S. Patent No. 2,647,088, U.S. Patent Office, Washington, D.C.
- Gunderson, L.O. (1953). "Compounds for Altering Surface Characteristics of Liquids," U.S. Patent No. 2,630,440, U.S. Patent Office, Washington, D.C.
- Denman, W. (1954). "Foaming in Boilers," *Industrial & Engineering Chemistry* 46(5), pp. 992-994.
- Denman, W.L. (1955). "Method of Inhibiting Foam Formation in Steam Generating Systems," U.S. Patent No. 2,727,867, U.S. Patent Office, Washington, D.C.
- Cheng, L.; Mewes, D.; Luke, A. (2007). "Boiling Phenomena with Surfactants and Polymeric Additives: A State-of-the-Art Review," *International Journal of Heat and Mass Transfer* 50(13), pp. 2744-2771.
- Raza, M.Q.; Kumar, N.; Raj, R. (2018). "Wettability-Independent Critical Flux during Boiling Crisis in Foaming Solutions," *International Journal of Heat and Mass Transfer*, 216(Part A), pp. 567-579

Endnote

^ATGWT is the company mentioned in the text that has developed its own instruments (patent pending) to simulate boiler conditions.



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