

## ORGANIC PLANT CYCLE TREATMENT CHEMICALS

AN INTERVIEW WITH **WOLFGANG HATER**  
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[...]

In the last eight months, nine papers have been published in PowerPlant Chemistry journal dealing either exclusively or largely with the behavior of organics in the fossil plant cycle.

[...]

The PowerPlant Chemistry editor has received many e-mail requests asking for more detailed information. Although we would like to respond to all these e-mails as correctly and precisely as possible, we do not possess all the necessary data.

For this reason, we have decided to contact major suppliers of organic plant cycle treatment chemicals and ask them the questions that we have received from our readers. This time, our interviewee is Wolfgang Hater representing BK Giulini GmbH.

### QUESTION #1:

First we would like to thank you for your willingness to respond to representative questions from our readers. Let us start with the most frequently asked question: Who are the typical users of your chemicals? Are these public and private utilities, industrial steam and power generators, or operators of combined cycle units with heat recovery steam generators?

### Answer #1

First of all, I would like to thank PPChem to give us the possibility to explain our technology to their readers. As not everyone may be familiar with the range of chemical additives that BK Giulini is offering I would like to briefly introduce our technology of film forming amines for steam generators, which we are offering under the brand name 'Cetamine® V'. In this interview, I am not dealing with the conventional treatment programs for steam generators (Ferrolux®).

Film-forming amines, often referred to as polyamines or fatty amines, are defined chemical substances that belong to the oligoalkylamino fatty amine family. The general chemical formula is  $R^1-[NH-(R^2)-]_n-NH_2$ , where  $n$  is an integer between 0 and 7,  $R^1$  is an unbranched alkyl chain with 12 to 18 carbon atoms and  $R^2$  is a short-chain alkyl group that usually contains 1 to 4 carbon atoms. The simplest representative is the known octadecylamine ( $n = 0$ ,  $R^1 = C_{18}H_{37}$ ), our treatment programs therefore contain film-forming amines in which two or more amino functionalities are present, e.g. oleyl propylene diamine ( $n=1$ ,  $R^1 = C_{18}H_{35}$ ,  $R^2 = C_3H_6$ ) or stearyl dipropylene triamine ( $n = 2$ ,  $R^1 = C_{18}H_{37}$ ,  $R^2 = C_3H_6$ ). For food related applications, that require a FDA §173.310 conformity, we provide Cetamine V 217 based on oleylamine ( $R^1 = C_{18}H_{35}$ ;  $R^2 = C_3H_6$ ), that has been certified by an independent third party law-firm, that has the expertise in evaluating food contact substances.

In general, these film-forming amines are not added as individual substances but rather in combination with alkalis amines such as cyclohexylamine, in order to adjust the pH of the boiler water and the condensate to the necessary value. At the same time they serve to provide the necessary storage stability of the formulations. As a result, there is often no need for additives whose sole function is to stabilise the formulations. Further information on the properties can be taken from the paper 'The Chemistry and Properties of Organic Boiler Feedwater Additives Based on Film-Forming Amines and Their Use in Steam Generators' by Wolfgang Hater, Niels Rudschützky, and David Olivet, PPChem 2009, 11(2), 90–96.

The typical users of our chemicals for steam generators are industrial steam and power generators, district heatings as well as CHP plants. Especially in plants with complex steam systems and with changing operational conditions, the film forming amine technology is able to prove its strength. Due to its volatility of the film forming compound a protective layer is formed on all the surfaces in the whole system, that is resistant against short term upset conditions, e.g. oxygen leakage into the condensate, supply of condensate of poor quality from external users.

For small boiler systems it is also advantageous, that the film forming amines are ready to use one-drum solutions, avoiding the need to handle several chemicals and frequent adjustment of dosing as well as preparation of dosing solutions. A faulty preparation of dosing solutions is a main reason for a poor treatment result. These boilers often don't have sophisticated water preparation systems and sometimes are operated even without degassing units.

On the other hand public utilities are not the major target group for the application of film forming amines. However, we are treating some utilizes with good success. Generally, the utility had been facing severe problems that it couldn't manage with the conventional treatment programs. In this case a very careful follow-up of the treatment is essential.

### QUESTION #2:

What are the largest units in which your products are in use? Can you give us some examples? Please state either the unit capacity in MW or the steaming capacity in t/h.

### Answer #2:

A few examples of bigger plants treated with our film forming amines:

Type of plant	Operational pressure [bar]	Steam capacity [t/h]
CHP plant	113	250
TLE (petrochemistry)	125	350
Power plant	145	670
Petrochemistry (field trial)	210	170
District heating	70	340
Power plant	135	660
Gas purification	30	400
Paper mill	90	120

### QUESTION #3:

Are there any restrictions (for example steam pressures and temperatures) with respect to the applicability of your products? It is generally known that different organic chemicals behave differently, e.g., at high temperatures. Some organics are relatively stable; others are subject to fast decomposition. We assume that, for this reason, it will not be very easy to answer this question. Nevertheless, please state any such limits and use the international (SI) units. Although most readers of our journal come from the United States, a considerable part of our readership comes from countries in which the use of US units is not common.

### Answer #3:

I fully agree on your comment. It is not possible to give the one or the other exact limit for a technology, as the operational conditions and plant layout of steam generators show a wide variety depending on the plant.

The highest temperature of a steam generator usually occurs in the superheater unit. Currently, we are operating plants with superheater temperatures up to 540 °C with good results. A lab study of the thermal stability of the film forming component oleylpropylen

diamine showed no significant decomposition up to maximum tested temperature of 500 °C: TGA analysis proof the stability up to the boiling temperature of the material at around 250°C. Above the boiling temperature TGA can't provide any information. Therefore, we have studied the thermal stability of the film forming component by pyrolysis GCMS up to a temperature of 500 °C and the resulting spectra are identical with the one obtained at 60°C showing, that no decomposition has taken place.

Although these results obtained in the laboratory can't be transferred directly to the conditions in a steam generator, these results together with the positive field experience give a strong indication that the key component does not significantly decompose inside a steam generator up to 540 °C.

The maximum pressure and steam temperature at which treatment with film-forming amines is appropriate have yet to be determined. In general, their use at pressures up to 80 bar is regarded as unproblematic, the experience which has been acquired at higher operating pressures is not

yet sufficient to give a full 'green light'. At this pressure range a close follow-up by our service engineers is recommended, especially in the start-up phase of the treatment.

The maximum operational pressure of a steam generator, where our film forming amine technology is applied to, is 210 bar. After half a year the treatment result was regarded as successful and the trial prolonged.

#### QUESTION #4:

We have almost forgotten to ask you whether your additives are used exclusively in units or plants with circulation steam generators or are also used in units or systems with once-through steam generators. Please comment.

#### Answer #4:

The experience in once-through steam generators treated with film forming amines is very low. We have started a field trial in a 210 bar Benson boiler at the end of 2008. The major objective of the trial is to stop or at least reduce the further growth of the magnetite layer, which had grown during the treatment with a conventional treatment program (hydrazine and ammonia).

In the treatment review after app. six months of treatment with film forming amines, our customer preliminarily judged the results as positive and decided to prolong the trial.

#### QUESTION #5:

In many discussions about the pros and cons of organic additives, one topic is often very controversial – the possible negative effects of decomposition products of organic additives on steam turbine disks and blades. This is clearly not relevant for back-pressure turbines. However, it is supposed that the presence of decomposition products in early condensate or films on the surfaces of blades and disks of condensing turbines may result in corrosion or cracking of these turbine parts. A two-part question in this connection: Are your products also applied in plants with condensing turbines, and – if the answer is YES – what is your or your customers' experience?

#### Answer #5:

Indeed, our products are also applied in systems with condensing turbines. Two examples have been published in the literature:

- 1) Three Years of Experience with Polyamines in the High Pressure Steam System of a Naphtha Cracker; Roy van Lier, Gerard Janssen, and Jo Savelkoul; PPChem 2008, 10 (12), 696
- 2) 'The Chemistry and Properties of Organic Boiler Feedwater Additives Based on Film-Forming Amines and Their Use in Steam Generators' by Wolfgang Hater, Niels Rudschützky, and David Olivet, PPChem 2009, 11(2), 90–96.

Although the experiences are consistently positive, we are facing the issue, that the acid conductivity measured normally exceeds the value of steam for steam turbines specified by VGB R 450 L. The normal range of acid conductivity is between 0.2 and 0.6  $\mu\text{S}/\text{cm}$ , when the system is treated with film forming amines.

A major concern of the increased conductivity in the steam is the possible masking of acidic compounds that may have formed by thermal decomposition of the additives or by incorporation of any pollutant into the system, e.g. humic acids in the feed water. These acidic compounds can lead to the dangerous so called early condensate corrosion, which could severely damage the turbine or other parts of the steam generator.

Studies from an operator of an industrial steam generating system have shown, first, the occurrence of this phenomenon, when morpholin was applied in the steam system, and second, that after the application of a film forming amine technology no first condensate corrosion was found any more (Überwachung der Korrosion des ersten Kondensats in industriellen Dampfsystemen;

Savelkoul J., Janssen P., Verhoef H.; PPChem 2001, 3(6), 366). Morpholin is not used in our Cetamine range.

### QUESTION #6:

High-pressure utility cycles with circulation boilers are very often equipped with condensate polishers, and cycles with once-through steam generators almost always. Do you have any experience with respect to the possible interactions between organic additives or their decomposition products and ion exchange resins? It is expected that different amines may affect the ion exchange resins in different ways. For example, film-forming amines are suspected of irreversible adsorption on polisher resins. Can you comment on this issue?

### Answer #6:

Although from the practical experience with the application there is no evidence that a condensate polishing unit is deteriorated by a film forming amine based program, there are only very few data reported on the behavior of amines on polisher resins.

Therefore, we have started a research program together with an external specialist on ion exchange units in order to investigate more deeply and under fully controlled conditions the interaction of amines with condensate polishing units. Two different mixed bed ion exchangers were loaded in a pilot simulation unit with DI-water treated with a commercial product, based on film forming amine and alkalizing amines. The residual free film forming amine level before the passage through the mixed bed was app. 0.5 g/m<sup>3</sup>.

The study is not completed, yet. So far the following key learnings have been obtained: The alkalizing components are almost quantitatively removed by the resins until the breakthrough. The alkalizing amines are completely removed from the resins by the normal regeneration.

In contrast to this, the film forming amine component, which is also completely eliminated by the resins, is practically not removed from the resins by the normal regeneration. In a second loading/regeneration cycle a release of film forming amine from a resin to the effluent was observed after the breakthrough of the alkalizing amines, leading to higher film forming amine concentration in the effluent than in the feed. This indicates, that the mechanism of binding of the film forming amine compound to the resin is different from the alkalizing amine. It seems, that after the loading with film forming amine once is completed, the excess is removed from the resin by the alkalizing amines. This finding would correspond to the field experience, that polisher units can be operated in the normal way for many years, when film forming amines are applied.

I would like to point out, that the study is still ongoing and some results need verification.

In paper 1 mentioned in answer #5 data are given on the influence of film forming amine dosing on the regeneration frequency. In this case the regeneration interval of the cation exchanger could be significantly increased after a change to a treatment with film forming amines. However, this might reflect both the effect of the amines and the reduction of the steam/condensate conductivity.

It should be emphasized, however, that there is a serious risk of clogging the polisher, if the film forming amine is overdosed. In this case a black and sticky deposit may form in the polishing unit and other parts of the steam generator, e.g. in filters. Therefore, it is important to maintain the free residual amount of film forming amine in the specified range of 0.2 to 0.5 g/m<sup>3</sup>. In case of proper dosage, we never observed any clogging of the polishers.

### QUESTION #7:

From a great many industrial plants it has been reported that the use of organic plant cycle treatment chemicals has markedly reduced corrosion product generation and transport in often very complicated systems with large steam and condensate networks. Who are the typical

industrial users of your additives and what are the typical results of their application of your products? Please give us some examples.

**Answer #7:**

Due to its volatility the film forming compound enables the formation of a protective film and thus corrosion protection of the whole steam and condensate line. We normally observe very low iron levels in the condensate when the steam generator is treated with film forming amines.

During a certain period after the change from a conventional treatment to a program based upon film forming amines a slight increase of the iron levels in the condensate may be observed. This increase, however, is temporary – it usually lasts between a couple of days and some months – is due to the high surface activity of the film forming components, that can lead to a soft cleaning effect. In order to avoid any risk, our start-up procedure should be carefully followed.

Some examples:

- The steam generators of a huge municipal district heating system were treated with a conventional program (oxygen scavenger, phosphate, ammonia). Due to the high complexity of the system (several hundred km of steam and condensate lines) with open tanks having contact to air corrosion in the system couldn't be sufficiently prevented, reflected by poor control of the pH and an average iron

level in the condensate of 0.9 g/m<sup>3</sup>. Four months after the change to film forming amines program the pH in the condensate had stabilized around 8.3 and the average iron level was reduced to 0.4 g/m<sup>3</sup>.

- In a gas purification plant the steam generator traditionally was treated by solid alkalization and hydrazine as oxygen scavenger and passivating agent. The treatment results were satisfying, however, the customer wanted to replace the toxic treatment chemical. After the start-up of the treatment with film forming amine there was a slight increase of the iron in the condensate (0.03 to 0.06 g/m<sup>3</sup>) for a three months period. Thereafter, the iron level came down again to around 0.01 g/m<sup>3</sup>.
- In almost all applications, where a treatment program based on sulphite and phosphate was replaced by a treatment with film forming amines we see a significant decrease of the iron concentration in the condensate from 0.5 to 1.0 g/m<sup>3</sup> to 0.1 g/m<sup>3</sup> and below. Examples are coming from various industries, e.g. pharmaceutical industry, food processing, aerospace, paper mills.

**QUESTION #8:**

Two types of corrosion seem to be very difficult to cope with: flow-accelerated corrosion (appearing in both variants, single-phase and two-phase) in condensate and feedwater trains in all plant cycles, and corrosion of ducts and tube entries in air-cooled condensers. What is your assessment with respect to the mitigation or avoidance of these corrosion processes with the help of organic plant cycle treatment chemicals?

**Answer #8:**

Flow accelerated corrosion is a phenomena occurring mainly due to high water and steam velocities. Since the film forming amines form a protective layer on the metal surface it could be imaginable that there might be a reduction of FAC under certain conditions.

Substantiate studies under controlled conditions on the influence of film forming amines on this kind of corrosion to my knowledge have not been carried out so far. BK Giuliani would be happy to discuss how to design and eventually participate to such kind of study.

**QUESTION #9:**

We have not yet addressed the most delicate issue, the cation conductivity increase in steam, condensate and feedwater when organic additives are applied. This issue is very often adduced

by all those opposed to organic additives. This point of view is absolutely understandable – cation conductivity monitoring is the most important tool for the plant cycle chemistry surveillance. An increase due to the presence of decomposition products of organics may mask contamination of the cycle by salts of strong inorganic acids. What is your opinion or experience? Could you please state the typical cation conductivity of the steam in cycles in which your additives are in use? Please also comment on this exasperating monitoring issue.

**Answer #9:**

I think you are referring mainly to the specification of the VGB guideline about the acid conductivity in the steam and condensate before steam turbines. Indeed, we know that the VGB spec of acid conductivity, especially in the steam normally can't be met when a treatment program based on film forming amines is applied. The acid conductivity typically is between 0.2 and 0.6  $\mu\text{S}/\text{cm}$ . The cases study at a CHP plant is an example for this (c.f. paper mentioned in answer #1). This range is also given in paper 1 mentioned in answer #5. We should, however, not forget, that a poor feed water quality (e.g. high TOC) or oxygen ingress into the system lead to higher acid conductivity levels in the steam due to the decomposition of organic components such as polysaccharides.

A similar range, i.e. 0.3 – 0.6  $\mu\text{S}/\text{cm}$  is also mentioned in the contribution 'Zum Verhalten von Polyaminen im Wasserkreislauf', Frahne D., Blum T., presented at the PPChem seminar "Organische Konditioniermittel für den Wasserkreislauf" in Heidelberg on 22./23.05.2007. The authors also give a possible explanation for the increased conductivity: the formation of carbamic acids by reaction of amines with carbon dioxide.

Although this is a plausible explanation, there is no straightforward analytical proof until now due to the very low concentrations and the instability of the carbamic acids.

As a consequence, the reason, why the acid conductivity in the steam/condensate normally is higher than the specified value from the VGB-guideline is not completely known. Generally it is assumed, that thermal decomposition of the film forming component in the steam generator might contribute to it. Our studies on the thermal stability (cf. answer #3), however, didn't show any evidence of a decomposition.

The VGB R 450 L indicates in a remark, that carbon dioxide in the steam/condensate should be taken into consideration when measuring the acid conductivity.

Therefore, on the VGB conference 'Chemie im Kraftwerk' 2007 in Rostock it was suggested to measure the acid conductivity after degassing in order to eliminate any effect of carbon dioxide (Cation conductivity monitoring performance during start-ups', Rziha M., Wuhrmann P., conference proceedings). This method, however, is hardly used until now. Therefore, comparative data between acid conductivity and degassed acid conductivity are not available.

A major concern of the increased conductivity is the possible masking of acidic compounds that may have formed by thermal decomposition of the additives or by incorporation of any pollutant into the system. These acidic compounds can lead to the dangerous so called first condensate corrosion, which could severely damage the turbine or other parts of the steam generator. This topic has already been addressed in answer #5.

One important measure to limit the acid conductivity in the condensate is for sure the careful control of the residual free film amine. A minimum amount of detectable free film forming amine compound in the condensate is sufficient to ensure the formation of the protective layer in the system. With the method of analysis provided by us the amount of residual free film forming amine can be safely determined down to 0.2  $\text{g}/\text{m}^3$ . The amount of free amine shouldn't exceed 0.5  $\text{g}/\text{m}^3$

It should be noted, that the acid conductivity requirement from VGB R 450 L is sometimes also exceeded, when a conventional treatment program is applied. In these cases often other problems have occurred, such as increased iron levels in the condensate lines or in the boiler. This has often been one major reason to switch the treatment concept to a film forming amine based one.

We have come to the end of this interview. What is the most important additional message that you would like to deliver to our readers? Any technical or scientific-based information is welcome.

### FREE SPACE FOR YOUR STATEMENT

'Organic Plant Cycle Treatment is Becoming More Attractive'. This was the title of a paper summarising the contributions of a seminar organised by PPChem in 2007 in Heidelberg (Organic Plant Cycle Treatment is Becoming More Attractive; Bursik A., PPChem 2007, 9(6), 358, where a lot of the questions asked here were intensively and controversially discussed.

The general conclusion was, that the film forming amine technology is looked upon as an interesting alternative treatment program especially for industrial steam generators. Application of this technology is driven mainly from experience, which is a good guidance, but to less extent from science, i.e. that there is a lack of basic data about the behaviour of film forming amines.

Although the film forming amine technology is a safe and good alternative if applied and serviced properly, our company decided to launch some research projects in order to address some of the critical issues that had come up.

1. Basic data on filming properties of film forming amines  
The film formation of film forming amines by electrochemical impedance spectroscopy showed a clear dependence of the filming ability on the chemical structure (Study of efficiency and stability of film forming amines (FFA) for the corrosion protection of the carbon steel in water circuits; Foret C., Stoianovici G., Chaussec G., de Bache A., zum Kolk C., Hater W.; proceedings of the EUROCORN, Edinburgh 2008).
2. Determination of distribution ratio and average surface coverage by film forming amines  
In a pilot boiler the distribution ratio in dependence on the operational pressure was determined for different film forming components. Furthermore, the average surface coverage was determined by analyzing the balance between total amines dosed and free residual amine in the equilibrium. Thereof, it could be stated, that the surface coverage by film forming amine in a steam generator in practice is below 0.5 g/m<sup>3</sup> and thus is negligible compared to the normal magnetite layer.  
First data were published on the 15<sup>th</sup> ICPWS (Film forming amine technology for steam generator treatment: properties, standardisation issues and field experiences; Hater W., Olivet D., proceeding of the 15<sup>th</sup> ICPWS, Berlin 2008). A more comprehensive study will be presented during the VGB-conference 'Chemie im Kraftwerk' in Dresden this year.
3. Interaction of film forming amine with condensate polishing units  
This study is ongoing and some results have already been discussed in answer #6.
4. Behaviour of Filming Amines in Steam Boilers  
A major objective of the research cooperation with the University of Rostock is the thermo-technical characterization of physicochemical processes on the surface of boiler tubes treated with conventional treatment programs and film forming amine.  
The research confirmed the result obtained in an earlier project, that there is no impact of the film forming amine on the burning-out type I. Systematic measurements of the heat transmission coefficients in dependence of imposed heat flux showed markedly higher heat transmission coefficients for tubes treated with film forming amine compared to solid alkalization with phosphate.  
Furthermore, with the film forming amine treatment the magnetite layer reached its stationary state in significantly reduced time.  
Results of this cooperation will be presented on the PPChem seminar 'Chemie im Wasserkreislauf' in October in Stuttgart as well as on the VGB-Conference 'Chemie im Kraftwerk' in Dresden.

Furthermore, we want to address the most important issue, the acid conductivity in the steam of steam turbines and possible decomposition of the chemical additive. Since it is practically impossible to study this under practice-like conditions in the laboratory, BK Giulini is intending a research cooperation with the Technical University Dresden, that will operate a small scale power plant (gas turbine with steam injection analogous to the CHENG process) for research and training purpose. It will also be equipped with a steam turbine and superheater. Herewith we

intend to obtain e.g. reliable data of the degassed acid conductivity and on a possible decomposition of the film forming amines.

Organic cycle chemistry based on film forming amines is a powerful technology due to its specific properties, mainly the protection of the whole system against corrosion. For many operators of this technology the driven force to apply it has been technical problems, which they faced, when they were using conventional programs.

Another advantage of film forming amines is its efficiency for wet lay-up of boilers and heaters. Furthermore, they can be used for pressure tests and boiling-out of installations, the latter is described in the VGB Guideline-R 513e '*Internal Cleaning of Water-Tube Steam Generating Plants and Associated Pipework*'.

As for all technologies there are also limitations for film forming amines and sometimes even obstacles from tradition. The major guidelines for steam generators give only very general recommendations for film forming amines. We are convinced that our research efforts will provide a better understanding of the phenomena occurring in the steam generator and help to finally implement specifications for the quality of water and steam also for this technology.

We greatly appreciate your taking time out to participate in this interview. Our readers will certainly be very interested in what you have had to say. Thank you very much!

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