



Rhodimet®

TECHNOLOGY - LIQUID - CORROSION - MIXER - STEEL



CORROSION IN THE MIXER BY LIQUID METHIONINE: MYTH OR FACT

Ivan Gaytan, Adisseo Technology Development Engineer / ivan.gaytan@adisseo.com

Jérôme Lamoine, Adisseo Product Application Technologies Development Manager. / jerome.lamoine@adisseo.com

Corrosion is a spontaneous phenomenon in the feed mill and liquid ingredients have long been considered as aggravating factors. Studies conducted for Adisseo by independent laboratories prove that the liquid ingredient D,L-methionine hydroxy (Rhodimet® AT88) is not such a threat for equipment.

Corrosion is a major concern for the feed mill manager. It reduces the equipment's lifespan and increases maintenance interventions. Because this phenomenon correlates to the presence of water, there is a belief that the presence of liquid ingredients, particularly acids, is the cause of corrosion. This is a mistaken belief and

industry researchers point to several parameters that influence the risk of corrosion. These parameters include characteristics of the feed and the concerned liquid, the application method, as well as environmental conditions. Controlling these parameters with good practices substantially prevents corrosion.



Corrosion is a spontaneous process

Corrosion is a complex, spontaneous phenomenon that occurs in normal conditions (figure 1) and involves several factors, such as temperature, humidity, pH, etc., (Wei Han, 2007). The reaction happens when an oxidant reduces by capturing electrons from a metallic surface. In neutral water, dissolved oxygen takes the electrons and reduces in hydroxide ions. The oxidized metallic atoms will dissolve and often react with hydroxide ions to precipitate as ferrous hydroxide ($\text{Fe}(\text{OH})_2$) then ferric hydroxide ($\text{Fe}(\text{OH})_3$), also known as rust (figure 2). In a low pH environment, the reaction takes place with the free protons within the acid. These reactions are thermodynamically possible because the reduction potential of the couples $\text{O}_2/\text{H}_2\text{O}$ and H^+/H_2 is higher than that of the metals composing the steel alloy (M. Pourbaix, 1974).

However, even if this oxidation happens spontaneously, what is important is the speed of the reactions that depend mainly on the conductivity of the solution, its concentration in oxidants or their activity (pH, dissolved oxygen), and its temperature. The materials composing the contact surface will also play an important role since they may confer the ability to form a protective layer. These parameters may significantly slow the corrosion rate.

For example, indirect contact an aqueous solution of sulfuric acid at 20°C with a concentration of 0.5% and a pH of 1 will corrode carbon steel at a rate of more than 1mm per year (L. Hasenbert, 1975). In contrast, **D,L – methionine hydroxy (D,L-HMTBA)**, an organic acid with higher concentration (88%), a low pH and at the same temperature, **will permit a speed of only $24\mu\text{m}/\text{year}$ for mild steel (table 1), which means it would take 42 years to corrode 1mm of surface.**



Figure 1, after (Wei Han, 2007): Scanning Electron Microscopy image of the surface of a steel plate exposed to atmospheric conditions for 5 days.(1)

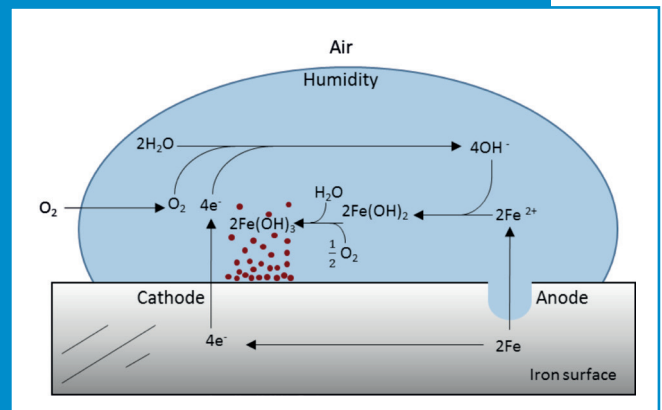


Figure 2: Mechanism of general corrosion in neutral aqueous conditions (2)

The lower conductivity of D,L-HMTBA results in a lower corrosion rate by reducing the activity of the cathode zone (electron transfer), and the dissolution equilibrium in the anode. This tendency is confirmed by the UN test C.1 conducted for Adisseo by an independent certified laboratory (see “liquid methionine exempt from class 8 - corrosive substances”).

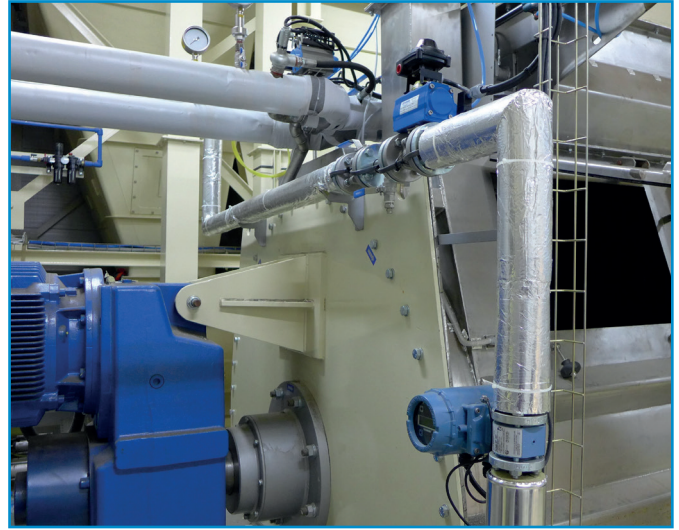
1- Highlighted we can see the signs of the first stages of corrosion

2- Humidity in the atmosphere is sufficient to form a layer of adsorbed moisture allowing corrosion. Ferric hydroxide is a metastable face that might rearrange into either goethite $\alpha\text{-FeO}(\text{OH})$ or hematite $\alpha\text{-Fe}_2\text{O}_3$ depending on the pH of the solution

Choosing the right materials for D,L-HMTBA

In the feed mill, liquid methionine (D,L-HMTBA) is stored then dosed and transferred to the mixer where it is sprayed. Depending on the step being considered, different precautions must be taken.

When D,L-HMTBA is being stored or transferred, the employed material will be in permanent contact. In order to evaluate exposure conditions, trials were conducted for Adisseo by an independent laboratory specializing in corrosion control. The tests were performed according to the Standard Practice for Laboratory Immersion Testing of Metals (ASTM G31-72 R04) (figure 3). Mirror polished plates of mild steel and two classes of stainless steel (304L and 316L) were weighed and measured in order to calculate the exposure surface. Then, the metals were immersed in 500ml of pure D,L-HMTBA for a period of 168h. No degassing or oxygen reduction procedures were



performed and the amount of liquid was sufficient in order to avoid acid depletion or any other possible medium deterioration. The pH of the medium and the corrosion speed were controlled. Stainless and mild steel samples were conditioned at 25°C. Stainless steel plates were also tested at 55°C.

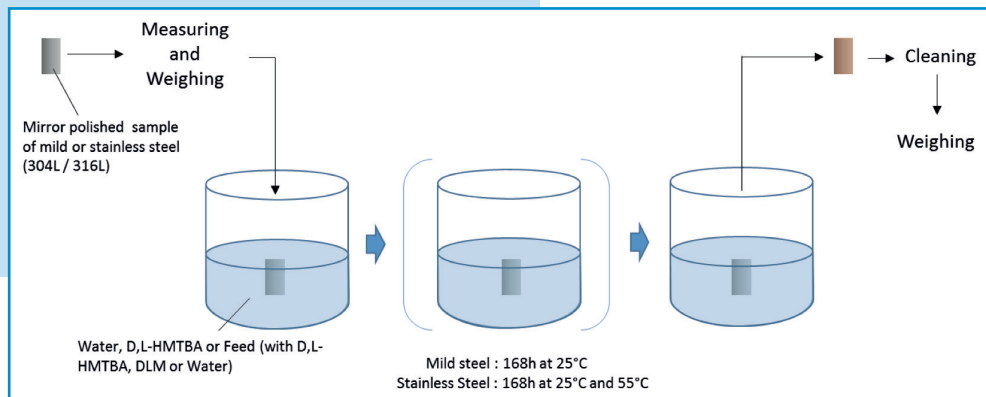


Figure 3: Steps for corrosion evaluation

Material tested	Temperature	Corrosion speed
Mild steel	25°C	24 µm/year (1mm in 40 years)
Stainless steel 304L	25°C	< 5µm/year
	55°C	< 5µm/year
Stainless steel 316L	25°C	< 5µm/year
	55°C	< 5µm/year

Table I: Test results for stainless and mild steel **in direct contact** with D,L-HMTBA at different temperatures. Both classes of stainless steel showed negligible corrosion inferior to the limit of detection

When the product is sprayed to the mash feed the conditions are quite different. In this case, D,L-HMTBA is loaded on a powder matrix composed almost entirely of organic matter (starch, fibers, proteins, etc.). These components are, by nature, highly absorbent. For example, starch has a liquid loading capacity of over 30% (H. Lankes, 2003). In such small doses of D,L-HMTBA, all liquid binds to the mash and becomes immobilized. This happens through capillary and layer adsorption, and formation of liquid bridges or liquid filled zones between feed particles (figure 4). These processes make the liquid unavailable for the corrosion reaction and therefore no special precaution may be needed.

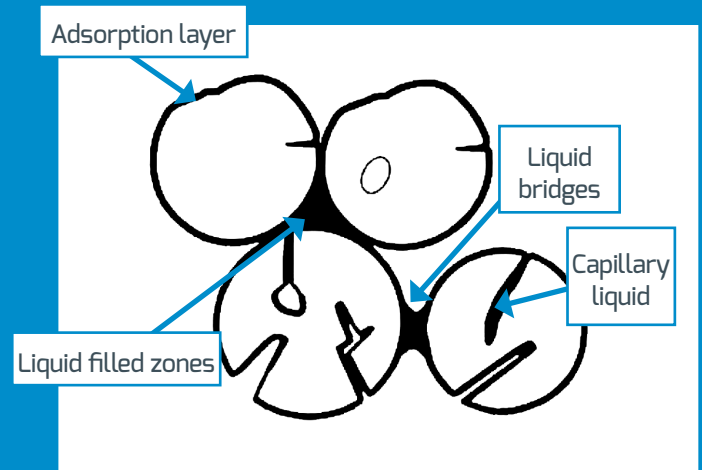


Figure 4 After (H. Lankes, 2003): Mechanisms of liquid retention by solid particles



Good application conditions for good results

When adding liquids to feed, the objective is to charge the mash homogeneously, avoiding the formation of agglomerates containing free liquid. To accomplish this, the nozzles, working temperature and pressure, and the sprayed zone within the mixer should be deliberately chosen within ideal parameters and the spray integrity maintained (J. Lamoine, 2015).

Feed was sprayed with D,L-HMTBA following these recommendations, in order to simulate mixer conditions. The product was then evaluated for potential corrosiveness, particularly for mild steel (figure 5). Trials were performed according to the ASTM G31-72 R04 standard. The following paragraph and chart elaborate test conditions and findings:

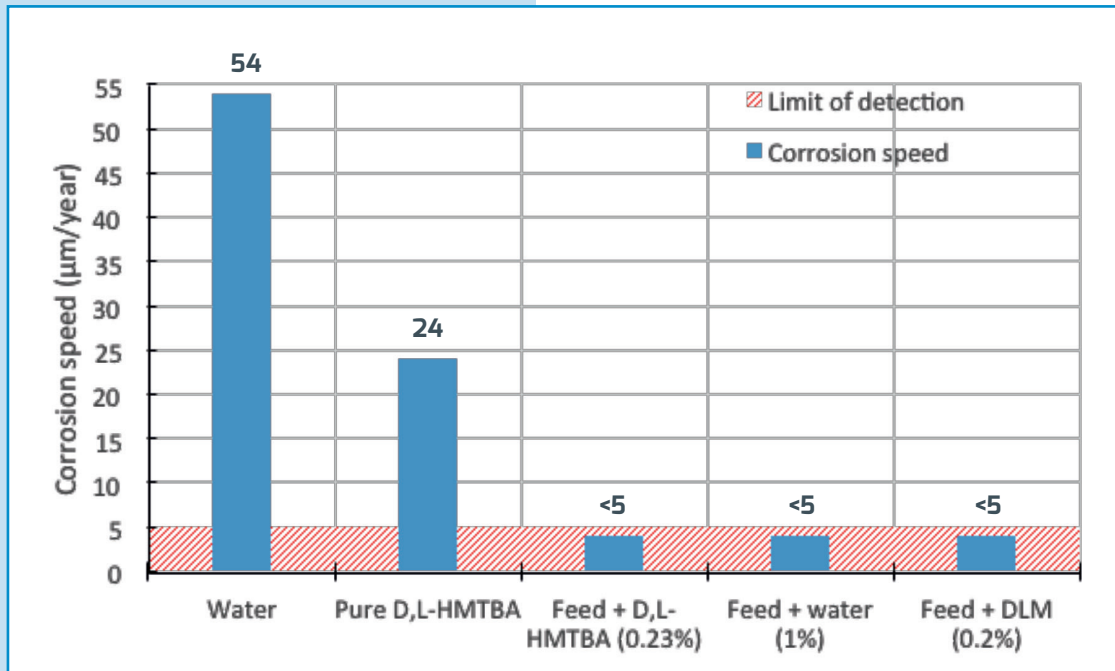
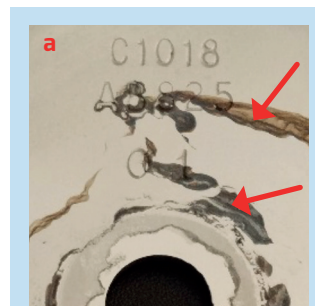


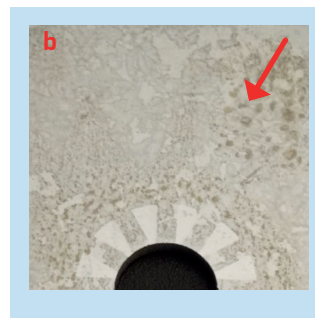
Figure 5 : Corrosion levels for mild steel when immersed in different environments.(3)

Mild steel plates were submerged in different environments at 25°C. Test duration was 168 hours, except for feed with D,L-HMTBA, which was tested for 334 hours. Speed values for D,L-HMTBA (figure 5 and 6b) were shown to be less than half of those recorded for water (figures 5 and 6a). It should also be noted that **when the mixer conditions are replicated, corrosion is negligible below the limit of detection of 5µm/year**, whether feed has added D,L-HMTBA (figure 6c), water or D,L Methionine (DLM). **This means that more than 200 years would be needed in order to wear out 1 mm of metal.** It can be inferred that corrosion will also be negligible for stainless steel in the same conditions.

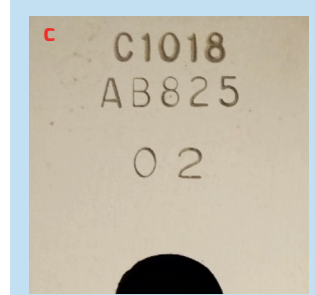
Figure 6: Mild steel samples after exposure to test conditions.



Water (4)



Pure D,L-HMTBA (5)



Feed with D,L-HMTBA (6)

3- Corrosion speeds less than the limit of detection cannot be estimated by the method employed in this study and are considered negligible.

4- Mild steel in aired water conditions at 25°C for 168 hours. Uniform corrosion (**) and deposits are observed (arrows). (*) Zone protected by the holding bar junction without corrosion.

5- Mild steel in pure aired D,L-HMTBA for 168 hours at 25°. A slight uniform corrosion is registered (arrows). (*) Zone protected by the holding bar junction without corrosion.

6- Mild steel in feed with D,L-HMTBA at 25°C for 334 hours. No corrosion observed.



Adisseo's expertise at the service of its clients

The trials exposed in this article demonstrate how D,L-HMTBA (liquid methionine) usage in the mixer does not lead to corrosion, regardless of building material (mild or stainless steel). Nevertheless, for any operation in which D,L-HMTBA is pure and in direct contact with a containing material for long periods of time (in pipes, pumps, injectors, etc.), Adisseo recommends to use materials such as stainless steel 316L. Through its DIM Program (Design Implement and Monitoring), Adisseo advises its clients to choose, install, and correctly calibrate their liquid methionine spraying equipment for safe operation and ideal outcomes.



Liquid methionine exempt from class 8 - corrosive substances

According to the UN Recommendations on the Transport of Dangerous Goods, corrosive substances (Class 8) are “substances which, by chemical action, will cause severe damage when in contact with living tissue, or, in the case of leakage, will materially damage, or even destroy, other goods or the means of transport”.

Trials to evaluate cutaneous irritation and corrosivity of liquid methionine showed that the substance is nonirritant nor corrosive for living tissue. They were done according to the OECD guideline No. 404 “Acute Dermal Irritation/Corrosion” 1981. In order to ascertain that liquid methionine could be considered non-corrosive, an UN metal corrosivity testing was performed following the method described on the UN Manual of Tests and Criteria, Test C.1 (table II). Both studies were performed by certified independent laboratories.

	Mild steel	Aluminium
Full submersed	0.09605	0.1223
Half submersed	0.11629	0.1133
Vapour space	0.00986	0.0015
UN limit recommendation	6.25	

Table II: Corrosion rate (mm/year) for steel and aluminum according to the UN test C.1 using liquid methionine at 55°C

Steel and aluminum samples exhibited corrosion rates of maximum 0.116 mm/year and 0.122 mm/year respectively. These values are 50 times inferior to the limit given by the UN regulations (6.25 mm/year). Liquid methionine is therefore exempt from classification as a corrosive substance of UN class 8, packing group III (according to the UN Transport of Dangerous Goods Recommendations).



References

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Figure 1: Reprinted from Corrosion Science, 49, Han, W., Yu, G., Wang, Z., Wang, J., *Characterisation of initial atmospheric corrosion carbon steels by field exposure and laboratory simulation*, 2920–2935, Copyright (2007), with permission from Elsevier.

Figure 4: Reprinted from Powder Technology, 134, Lankes, H., Sommer, K., Weinreich, B., *Liquid absorption capacity of carriers in the food technology*, 201–209, Copyright (2003), with permission from Elsevier.

