

SYNERGISTICALLY ACTIVE MIXTURE FOR USE AS AN OXYGEN
BINDER AND AS A CORROSION INHIBITOR IN AQUEOUS SYSTEMS

The present invention relates to a synergistically
5 acting mixture for use as oxygen binder in steam
generators, boilers, closed cooling systems, district
heating systems or heating circuits. Due to the oxygen
binding effect, the mixture simultaneously acts as
corrosion inhibitor.

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In industrial steam generators and boilers, closed
cooling systems, district heating systems or heating
circuits in which metals come into contact with water,
there is a risk of corrosion. The corrosion is caused
15 by the oxygen dissolved in water. This oxygen therefore
has to be removed, either by mechanophysical methods or
by chemical treatment of the oxygen. It is also
possible to combine the two methods by combining the
physical method simultaneously with the chemical
20 methods.

A known method is, for example, a combination of
thermal degassing and introduction of oxygen binders
such as the known hydrazine or sodium sulfite.

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Sodium sulfite, for example, is a compound which has
low volatility and whose reaction products contribute,
in combination with oxygen, to increasing the
conductivity of the boiler water and thus it causes
30 concentration, especially in plants which are operated
using deionized water. Use has therefore been made of
hydrazine because the reaction products do not react
with oxygen to increase the conductivity of the boiler
water.

However, hydrazine is, like the frequently used compounds such as hydroquinone or methyl ethyl ketoxime, problematical with regard to occupational hygiene because they are toxic and carcinogenic. To
5 replace hydrazine or ketoximes, some alternatives have been proposed over time:

Although US 3,983,048 describes the use of the compound hydrazine, arylamines are also used in catalytic
10 amounts in addition to hydrazine there. According to column 2, ortho- or para-phenylenediamines are used as arylamines. According to Table 1, the oxygen removal after 10 minutes is merely 95% when para-phenylene-
diamine is used. However, the toxicological concerns
15 were not able to be overcome completely by reducing the amount of hydrazine.

In US 4,728,497, hydrazine was replaced completely by aminophenols. As a class of compounds, they are less
20 toxic and in addition have a greater oxygen binding capacity. These compounds include, for example, 2,4-diaminophenol, 5-methyl-o-aminophenol, o- or p-amino-phenol and salts thereof, etc. It can be seen from Table 1 of this document that although the aminophenols
25 are more effective than hydrazine, viz. they can remove oxygen to an extent of up to 99% under comparable conditions, but on the other hand their reaction rate is relatively slow.

30 US 4,067,960 has proposed N,N-diethylhydroxylamine or salts thereof as alternative oxygen binders instead of hydrazine having a low hazard potential.

Thus, for example, compared to, inter alia, hydrazine or sodium sulfite, an improvement in the reduction of the dissolved oxygen from 96.8 to 98% was achieved when using N,N-diethylhydroxylamine/DEHA/. However, hydroquinone, benzoquinone or metal salts had to be used as catalysts in order to increase the reaction rate. However, the use of these compounds is undesirable or disadvantageous because of their toxicity. The metal salts used as catalysts, e.g. copper or cobalt salts, were also disadvantageous since they cause contact corrosion or in the case of a few cobalt salts are carcinogenic.

Furthermore, attempts have been made in the prior art to improve DEHA in combination with other, less toxic catalysts, especially because DEHA has a relatively slow oxygen binding effect, and EP 1 619 272 A1 has proposed heterocyclic compounds containing N-substituted amino groups, for example 1-amino-4-methylpiperazine, 1-aminopyrrolidine. However, a catalyst based on phenols containing a plurality of hydroxyl groups also had to be added to DEHA and the two compounds mentioned.

Reduction of oxygen in a mixture consisting of DEHA, 1-aminopyrrolidone and pyrogallol as catalyst gives, in Table 4 of EP 1 619 272 A1, a residual oxygen concentration after 20 minutes of 0.3 mg/l.

Neither the combination of DEHA with heterocyclic compounds containing N-substituted amino groups nor the sole use of aminophenols has brought a satisfactory result under the temperature and pressure conditions prevailing in steam generators in industry and

especially with regard to the requirement in respect of the speed of oxygen removal.

US 4,626,411 discloses a mixture consisting of three components a, b and c, where component a is present in a ratio to component c of from 10:1 to 1:10 and component b is present in a ratio to component c of from 10:1 to 1:100, for removing oxygen and reducing corrosion in boilers. Component a is a hydroxylamine compound, component b is an aromatic compound, for example aminophenol, and component c is an amine which serves to set the pH.

In column 5, lines 8 ff., it is stated that only the combination of neutralizing amine and hydroquinone brings about a very surprising effect on the increase in the reaction rate of N,N-diethylhydroxylamine with the oxygen.

However, the use of hydroquinones or the metal catalysts were not indicated for environmental reasons and from a toxicological point of view.

It has surprisingly been found that the use of a combination of only 2 components, namely a hydroxylamine, e.g. N,N-diethylhydroxylamine, as component a with an arylphenol derivative, e.g. 4-aminophenol, as component b in a ratio of from 6:1 to 1:1.5 displays a synergistic action in the removal of oxygen and thus also in reducing corrosion under the conditions of industrial steam generators, contrary to expectations. Compared to the individual components, this combination displays a significantly improved reaction rate, i.e. an increased degree of binding of

oxygen. The use of a third component, e.g. quinones or hydroquinones, could advantageously be dispensed with in this way.

- 5 The general structure or formula **(I)** of the hydroxylamines is:

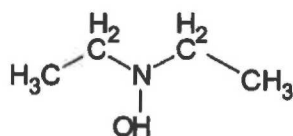
(I)



- where the substituents R^1 , R^2 can be identical or
 10 different and have the general formula
 $\text{C}_n\text{H}_{2n+1}$, where $n=1$ to 5, preferably from 1 to 2.

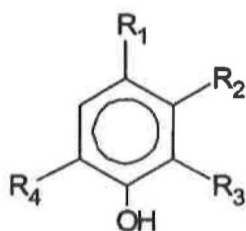
- The component a to be used according to the invention
 can be, for example, N,N-diethylhydroxylamine, which
 15 has the formula **(II)**:

(II)



The arylphenols of the component b have the general structural formula **(III)**:

(III)



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R_1 , R_2 , R_3 and R_4 are defined as follows:

R_1 , R_2 , R_3 and R_4 are each, independently of one another,

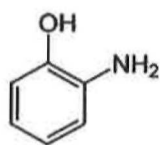
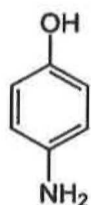
- 5 a) $C_mH_{2m+1}-N(-R_5)(-R_6)$ or
 b) OR_7 or
 c) R_8

where at least one R_1 , R_2 , R_3 and R_4 is a
 $C_mH_{2m+1}-N(-R_5)(-R_6)$ group. Here, R_5 , R_6 , R_7 , R_8 are
 each, independently of one another, C_nH_{2n+1} and n and
 10 m are integers from 0 to 4, preferably integers from
 0 to 2.

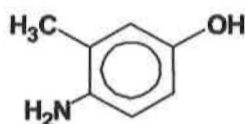
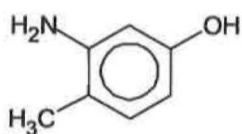
Preferred arylphenol compounds according to the
 invention are:

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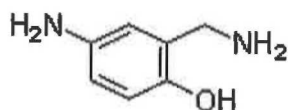
4-aminophenol and 2-aminophenol



3-amino-4-methylphenol and 4-amino-3-methylphenol



20 and 4-amino-2-(aminomethyl)phenol



The components a and b are present in a weight ratio to one another of from 6:1 to 1:1.5, in particular in a ratio of from 5:1 to 1:1.

- 5 According to the invention, particular preference is given to the combination of N,N-diethylhydroxylamine (component a) and 4-amino-3-methylphenol (component b).

Measurement method:

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The measurement of the oxygen concentration was carried out using the Sensor InPro 6800 measurement instrument from METTLER TOLEDO.

- 15 Mettler Toledo InPro 6800 sensors are employed for the in-line measurement of the oxygen partial pressure in liquids and gases.

The O₂ sensors InPro 6800 with integrated temperature sensor are employed for determining oxygen.

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Functional principle

- The InPro 6800 is based on the polarographic measurement of O₂ by the method of Clark, which can be summarized as follows:

25 The Clark sensor consists of a working electrode (cathode), counterelectrode/reference electrode (anode) and an oxygen-permeable membrane which separates the electrodes from the measurement medium.

30

A constant voltage is applied to the cathode via the transmitter in order to reduce the oxygen. The oxygen molecules diffuse from the measurement medium through the membrane to the electrodes and are reduced at the

cathode to which the voltage is applied. At the same time, oxidation in which the anode metal (silver) is released as silver ions into the electrolyte takes place at the anode. This makes the electrolyte
5 conductive and a current flows between anode and cathode (ion conductivity). The current generated is measured by the transmitter and is proportional to the oxygen partial pressure (pO_2) in the measurement medium.

10 Reaction at the cathode:



Reaction at the anode:



15 **Examples according to the invention:**

The oxygen binder is introduced into a flask which is filled with deionized water (conductivity $< 1 \mu S/cm$) and in which the supernatant amount of gas is minimal
20 and the oxygen concentration is measured by means of the electrode after defined points in time. During the experiment, the solution was blanketed with purified nitrogen.

25 The measurements were carried out at a temperature of $45^\circ C$.

The relative synergistic effect RS of the mixture is derived from the measured oxygen reduction $\Delta c_g[O_2](t)$
30 and the calculated oxygen reduction $\Delta c_b[O_2](t)$ at the point in time t of the measurement, in accordance with:

$$RS = \Delta c_g[O_2](t) / \Delta c_b[O_2](t) - 1.$$

If $RS > 0$, a synergistic effect is present; if $RS < 0$, an antagonistic effect is present.

The measured oxygen reduction $\Delta c_g[O_2](t)$ is given by the difference between the initial oxygen concentration $c_g[O_2](0)$ and the measured oxygen concentration at the respective point in time of the measurement $c_g[O_2](t)$:

$$\Delta c_g[O_2](t) = c_g[O_2](0) - c_g[O_2](t)$$

The initial oxygen concentration $c_g[O_2](0)$ was 7.1 mg/l.

The calculated oxygen reduction $\Delta c_b[O_2](t)$ is given by the weighted average of the measured oxygen reductions $\Delta c_g[O_2](A, t)$ and $\Delta c_g[O_2](B, t)$ of the two individual components a and b alone, in accordance with

$$\Delta c_b(t) = c(A)/60 \cdot \Delta c_g[O_2](A, t) + c(B)/60 \cdot \Delta c_g[O_2](B, t).$$

Here, $c(A)$ and $c(B)$ are the initial concentrations of the components a and b in the mixture.

Example 1: Mixture of N,N-diethylhydroxylamine and 4-aminophenol

Table 1 measured oxygen concentration $c_g[O_2]$ for mixtures of DEHA and 4-aminophenol

	DEHA	4-Amino-phenol	DEHA: 4-amino-phenol	$c_g[O_2]$ (2min)	$c_g[O_2]$ (4min)	$c_g[O_2]$ (6min)
	[mg/l]	[mg/l]		[mg/l]	[mg/l]	[mg/l]
$c_g[O_2](A, t)$	60	0	1:0	7	6.7	6.4
	50	10	5:1	6.2	4.8	5.3
	40	20	2:1	6.6	4.7	3.6
	30	30	1:1	6.3	3.8	2.4
	20	40	1:2	6.4	5.2	3.9

	10	50	1:5	6.1	3.7	2.6
$c_g[O_2] (B, t)$	0	60	0:1	6	2.3	1.1

Table 2: Relative synergy RM for mixtures of DEHA and 4-aminophenol

5 **Example 2:** Mixture of N,N-diethylhydroxylamine and 4-amino-3-methylphenol

DEHA	4-Aminophenol	DEHA:4-amino-phenol	RS (2min)	RS (4min)	RS (6min)
[mg/l]	[mg/l]	[mg/l]			
50	10	5:1	1.2	0.9	0.1
40	20	2:1	0.2	0.3	0.5
30	30	1:1	0.2	0.3	0.5
20	40	1:2	-0.4	-0.4	-0.2
10	50	1:5	-0.2	-0.2	-0.1

10 **Table 3:** measured oxygen concentration $c_g[O_2]$ for mixtures of N,N-diethylhydroxylamine (DEHA) and 4-amino-3-methylphenol

	DEHA	4-Amino-3-methylphenol	DEHA:4-amino-3-methylphenol	$c_g[O_2]$ (5min)	$c_g[O_2]$ (10min)	$c_g[O_2]$ (15min)
	[mg/l]	[mg/l]		[mg/l]	[mg/l]	[mg/l]
$c_g[O_2] (A, t)$	60	0	1:0	6.4	5.7	5.1
	57.14	2.86	20:1	6.2	5.6	5.4
	56.25	3.75	15:1	6.5	5.8	5.5
	54.55	5.45	10:1	6.4	5.6	5.2
	50	10	5:1	6	3.9	2.8
	40	20	2:1	5.3	3.8	2.6
	30	30	1:1	5.4	3.2	1.6
	20	40	1:2	6	4.5	2.6
	10	50	1:5	5.8	3.8	2.3
$c_g[O_2] (B, t)$	0	60	0:1	6.1	4.6	1.9

Table 4: Relative synergy RM for mixtures of N,N-diethylhydroxylamine (DEHA) and 4-amino-3-methylphenol

DEHA	4-Amino-3-methylphenol	DEHA:4-amino-3-methylphenol	RS (5min)	RS (10min)	RS (15min)
[mg/l]	[mg/l]				
57.14	2.86	20:1	0.1	0.0	-0.2
56.25	3.75	15:1	-0.2	-0.2	-0.2
54.55	5.45	10:1	0.0	-0.1	-0.2
50	10	5:1	0.2	0.9	0.6
40	20	2:1	1.3	0.8	0.4
30	30	1:1	1.0	0.9	0.5
20	40	1:2	0.3	0.2	0.0
10	50	1:5	0.5	0.5	0.1

A synergistic effect ($RS > 0$) is apparent for both mixtures of component a (DEHA) and component b (4-aminophenol; 4-amino-3-methylphenol) in a ratio of from 5:1 to 1:1.

The mixture according to the invention is generally introduced into the boiler feed water, for example in an amount proportional to the boiler feed water by means of a metering pump. The metering of the mixture is usually set so that a minimum concentration of N,N-diethylhydroxylamine can be detected in the condensate and in the boiler water. Monitoring of the degree of success can be effected by measurement of the iron content or by inspection of the plant components.

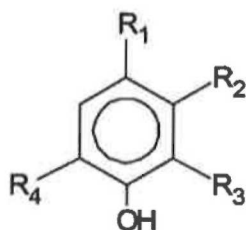
Claims

- 1) A synergistic oxygen binder consisting of the components a and b in a ratio of from 6:1 to 1:1.5, preferably in a ratio of from 5:1 to 1:1, wherein component a is a dialkylhydroxylamine having the general formula **(I)**

(I) HONR_2

and the substituents R can be identical or different, where $\text{R} = \text{C}_n\text{H}_{2n+1}$, where $n=1$ to 5, preferably from 1 to 2,

component b is an arylphenol derivative of the formula **(III)**

(III)

where R_1 , R_2 , R_3 and R_4 are each, independently of one another, a) $\text{C}_m\text{H}_{2m+1}-\text{N}(-\text{R}_5)(-\text{R}_6)$ or b) OR_7 or c) R_8 , where at least one R_1 , R_2 , R_3 and R_4 is a $\text{C}_m\text{H}_{2m+1}-\text{N}(-\text{R}_5)(-\text{R}_6)$ group and R_5 , R_6 , R_7 , R_8 each have, independently of one another, the formula $\text{C}_n\text{H}_{2n+1}$ and m and n are integers from 0 to 4, preferably from 0 to 2.

25

- 2) The oxygen binder as claimed in claim 1, wherein the components a and b are present in a weight ratio in the range from 6:1 to 1:1.5, preferably in

a ratio in the range from 5:1 to 1:1, in the water to be treated.

- 3) The oxygen binder as claimed in claim 1, wherein
5 component a is preferably N,N-diethylhydroxylamine (DEHA).
- 4) The oxygen binder as claimed in claim 1, wherein R_1 ,
 R_2 , R_3 and R_4 are each, independently of one
10 another, a) $C_mH_{2m+1}-N(-R_5)(-R_6)$ or b) OR_7 or c) R_8 ,
where at least one R_1 , R_2 , R_3 and R_4 is a $-NH_2$ group
and R_5 , R_6 , R_7 , R_8 are each, independently of one
another, C_nH_{2n+1} and m and n are integers from 0 to
4, preferably from 0 to 2.
- 15 5) The oxygen binder as claimed in claim 4, wherein
the arylphenol derivative is selected from among
n-aminophenols where $n = 2, 3, 4$, n-amino-m- C_oH_{2o+1} -
phenol or n-amino-m- $C_oH_{2o}NH_2$ -phenol, where $n = 2, 3, 4$
20 and $m = 2, 3, 4$ and n is not equal to m and o is an
integer from 1 to 4.
- 6) The oxygen binder as claimed in claim 6,
characterized in that the component b is preferably
25 4-aminophenol or 2-aminophenol or 4-amino-3-
methylphenol or 3-amino-4-methylphenol or 4-amino-
2-(aminomethyl)phenol.
- 7) The use of the oxygen binders as claimed in any of
30 claims 1 to 6 in industrial steam generators,
boilers, closed cooling systems, district heating
systems or heating circuits.