

Antiscale Efficiency of New Polymers Synthesized in Microwave Field

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Abstract—Cooling water systems endure pending exploitation the deposition of hard and adherent scales upon the thermal transfer surfaces.

This study proposes the microwave field technology for obtain antiscale agents, process used for first time in our country. We can specify several advantages of microwave heating comparatively with conventional heating methods: higher technological efficiencies, decrease of the reaction rate, the suddenly temperature control, significant decrease of the secondary compounds amounts resulted from the synthesis reactions.

New elaborated antiscale products we tested in laboratory for a fast evaluation of antiscale efficiency.

Keywords—Antiscalings agents, heat transfer, microwave field, new polymers.

I. INTRODUCTION

SCALE can be defined as an adherent deposit of inorganic compounds which is formed by precipitation of salts from water and crystal growth on heat transfer surfaces. Water used in industrial cooling systems comes from rivers, lakes or from underground reservoirs. Such water contains dissolved inorganic salts such as calcium, magnesium, etc. When this water circulates through the heat exchangers and cooling towers in a cooling system, a portion of the water is lost due to the evaporation. This increases the concentration of inorganic salts in the system. If the solubility of these salts in water is exceeded, precipitation of calcium carbonate, calcium sulphate and calcium phosphate will take place. As the salts precipitate on the internal surface of a cooling system, they form scale or deposits. The scale inhibits effective heat transfer, restricts the flow of the water, and promotes the development of underdeposit corrosion. Consequently, it is necessary to remove the scale by cleaning. Such cleaning is expensive because equipment must be shutdown, labor costs are incurred, and production is delayed. In view of these problems, preventing scale formation is preferred to scale

removal. Preventing scaling of industrial heat transfer equipment is essential to the efficient and economical operation of a cooling water system.

One of the most common scale deposits in circulating aqueous cooling systems is calcium carbonate. It normally results from the breakdown of calcium bicarbonate, a naturally occurring soluble salt. Calcium carbonate has a relatively low solubility and its solubility decreases with increasing temperature and pH. Thus, the rate of calcium carbonate deposition increases with increasing pH and temperature.

Scale formation can be inhibited by adding a sequestering or chelating compound to the water treatment system but this method is expensive and not customarily used.

More than 50 years ago it was discovered that certain compounds performed as highly efficient scale inhibitors. Such compounds are used in significantly lower than stoichiometric amounts and are known as "threshold inhibitors". Examples of threshold inhibitors are phosphonates and water soluble acrylic/maleic/sulfonic polymers or copolymers.

For the forming scales prevention was long time use the polyphosphates as antiscale agents. These are cheap, but present limited efficiency, their disadvantage consisting in their sensibility to temperature (they are hydrolysed to orthophosphates at temperatures higher than 90 °C). In the last years the use of these substances was significantly restricted. The most antiscale agents used seems to be the maleic acid's polymers. These prevent the precipitation, deposition and ripening of the dissolved material on metal surfaces and they prevent the growth of crystals through the system's structure distortion, so that a soft residue is formed, which do not adheres and do not increases on the metallic surfaces.

The scale's control is achieved through the addition of different agents which in principle can be divided in two categories:

-organic compounds with low molecular weight which check up the forming crystals rate, distort the forming of these and limit their increase. Between the most used additives of this type are the phosphonates with special efficiency in control of calcium carbonate, respectively calcium phosphate scale formation. It is important to notice that these inhibitors do not actuate on stoichiometric principles, one gram-equivalent of 2-phosphonobutane-1,2,4-tricarboxylic acid (PBTC) may successfully struggle 100-3000 CaCO₃ or Ca₃(PO₄)₂ gram-equivalent.

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-polymeric dispersers which are attached to the nucleating centers existing in solution, interfere with the crystals growth process and prevent the encrustment through her maintaining in suspension; this type of additives presents also efficiency to substoichiometric doses.

Both types of additives promote the formation of a soft scale, inadherent, which is easy removed from system through mechanical cleaning. Often, the both types of additives are utilised together, especially in cooling systems where the salts which form scales are more over the saturation concentration or when, as a result of high concentrations' action, the degradation of the phosphonates is strong.

In this paper, we propose a microwave field technology for obtaining new polymeric products with antiscaling action by polymerization reactions initiated through thermal decomposition of initiator.

The microwave heating presents more advantages comparatively with the conventional heating methods (water bath, steam, electric heating):

- produces an increase of the reaction rate by 10-1000 times;
- the heating is done in all volume as a result of the profundity penetration of the radiation and is not controlled by the thermal conductivity at surface;
- the energy selective adsorption does the drying process, especially the water removal, much more efficient;
- the suddenly temperature control, because the microwave's power can be electronic adjusted in one second;
- the process is "dry" because does not need additional medium for the heat transfer and does not emit smoke or combustion gases, which is better agree with the environmental requirements.

II. EXPERIMENTAL RESEARCHES

A. Preliminary Lab Researches

In order to select informative receivers on the strength of whom we can pass on systematic parameters studies having as result the achievement of products with antiscaling effect, we performed preliminary researches whose main purpose was the choice of the monomer type and eventually, the choice of the molecular mass controlling agent and/or of the utilizable initiator type. To this effect we attained a lab installation for the effectuation of polymerization reactions in microwave field.

Within the preliminary researches we have synthesized six types of water-soluble antiscaling (co)polymers, with different composition, from which we selected two types for parameters studies:

1. Maleic anhydride homopolymer (PMA) with the general formula shown in Fig. 1 (a).

2. Phosphino-acrylic homopolymer (PCA)

This product is constitutes from majority mixture of two compounds with the general formula presented in Fig. 1 (b).

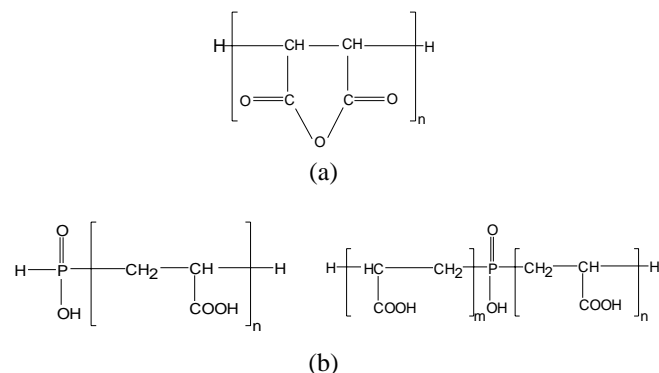


Fig. 1 The general formula of the selected antiscaling polymers

On the basis of the two selected product types, we have achieved samples of polymers for lab researches.

These samples have the following indicatives:

- **PCA** (*phosphino - acrylic polyacid*): dry substance = 50%; pH = 2;
- **PCA-M11** (*volumetric mixture 1:1 phosphino - acrylic acid - 2 - phosphonobutane - 1, 2, 4 - tricarboxylic acid*): dry substance = 50%; pH = 1.1;
- **PCA-M21** (*volumetric mixture 2:1 phosphino - acrylic acid - 2 - phosphonobutane - 1, 2, 4 - tricarboxylic acid*): dry substance = 50%; pH = 1.23;
- **PMA-M1** (*volumetric mixture 1:1 polymaleic acid - 2 - phosphonobutane - 1, 2, 4 - tricarboxylic acid*): dry substance = 55%; pH = 0.3;
- **PMN** (*polymaleic acid neutralized by sodium hydroxide*): dry substance = 40%; pH = 6.45.

B. Laboratory Experiments for Antiscaling Efficiency Evaluation

The present methodology is utilized for the quick lab evaluation of the antiscaling inhibitors efficiency. The test procedure has to base the assessment principle of the inhibitors capacity in the calcium carbonate and calcium sulphate precipitation prevention. The method's purpose is to differentiate between certain compounds with antiscaling inhibitor role and for to establish the optimum ratio of mixture necessary for the encrustment control.

The method principle consists in the preparation of a CaCO_3 solution in supersaturated state, the addition of antiscaling inhibitors in preestablished amounts, her maintaining in a predetermined period of time at a certain temperature and the remanent hardness determination. The chemical principle which stands at the base is the chemical reaction of the calcium carbonate or the calcium sulphate with EDTA (the sodium salt of the ethylene diamine tetra acetic acid). The reaction takes place in basic medium in the presence of the murexide.

As reaction medium for lab testing of the new inhibitors synthesized in microwave field we used industrial water from different industrial cooling plants. We have selected three

sources of water that have strong incrusting character because of their composition. This character is especially given by the calcium bicarbonate content of water (m alkalinity).

Water sources used for the lab experiments we symbolized during the researches as the water source 1, the water source 2 and the water source 3, having the chemical characteristic properties presented in Table I:

TABLE I
CHEMICAL PROPERTIES OF THE USED WATER

Indicators	Water source 1	Water source 2	Water source 3
<i>pH</i>	8.42	7.95	8.91
<i>Conductivity ($\mu\text{S/cm}$)</i>	1061	665	340
<i>Alkalinity (mval/L)</i>	3.3	4.2	4.04
<i>Total hardness (mval/L)</i>	8.3	4.18	8.0
<i>Calcium hardness (mval/L)</i>	3.0	4.16	4.2
<i>Chloride (mg/L)</i>	117.01	95.74	24.82
<i>Sulphate (mg/L)</i>	155	73.15	64.63
<i>Slurry (mg/L)</i>	2.75	0.95	2.65
<i>Organic matters (mg/L)</i>	11.37	3.47	8.53
<i>Iron (mg/L)</i>	0.073	0.099	0.05
<i>Aluminium (mg/L)</i>	0.0175	0.02	0.025
<i>Nitrite (mg/L)</i>	< 0.1	< 0.1	< 0.1
<i>Nitrate (mg/L)</i>	10	35	< 1.0
<i>Phosphate (mg/L)</i>	0.046	< 0.04	< 0.04
<i>Cuprum (mg/L)</i>	< 0.015	< 0.02	< 0.02
<i>Zinc (mg/L)</i>	< 0.1	< 0.1	< 0.1

The tests have been performed in water samples from each source previously presented, that were introduced in iodometric flasks. We dosed the antiscaling products at the concerted concentrations and then all the samples were held in drying chamber at constant temperature (71°C), for 72 hours. For the antiscaling efficiency evaluation we used blank assays, without antiscaling inhibitor. We have prepared two blanks from each water sample. One of them was introduced in drying chamber at the same time with the samples with inhibitors – warm blank, and the other was kept at ambient temperature – cold blank. After 72 hours, the samples have been taken out from drying chamber and warm titrated with EDTA.

Table II presents the results of the studies - antiscaling efficiency for the tested inhibitors.

Fig. 2 shows the experimental data obtained for the tested inhibitors in the three sources of water.

TABLE II
ANTISCALE EFFICIENCY OF INHIBITORS TESTING IN WATER FROM SOURCE 1, 2, AND 3

Scale Inhibitors	Concentration (mg/L)	Antiscale Efficiency (%)		
		Water Source 1	Water Source 2	Water Source 3
PCA	10	90.00	88.83	49.46
	20	93.33	90.10	51.35
PCA M11	5	30.00	53.75	39.47
	10	69.03	86.69	60.52
	20	85.78	98.20	65.78
PCA M21	5	66.36	34.85	39.47
	10	85.78	99.00	78.94
	20	91.37	99.26	84.21
PMA M1	5	56.36	75.62	44.73
	10	77.15	98.83	57.89
	20	92.38	99.04	73.68
PMN	12.5	95.00	71.42	43.01
	25	96.66	81.69	51.61

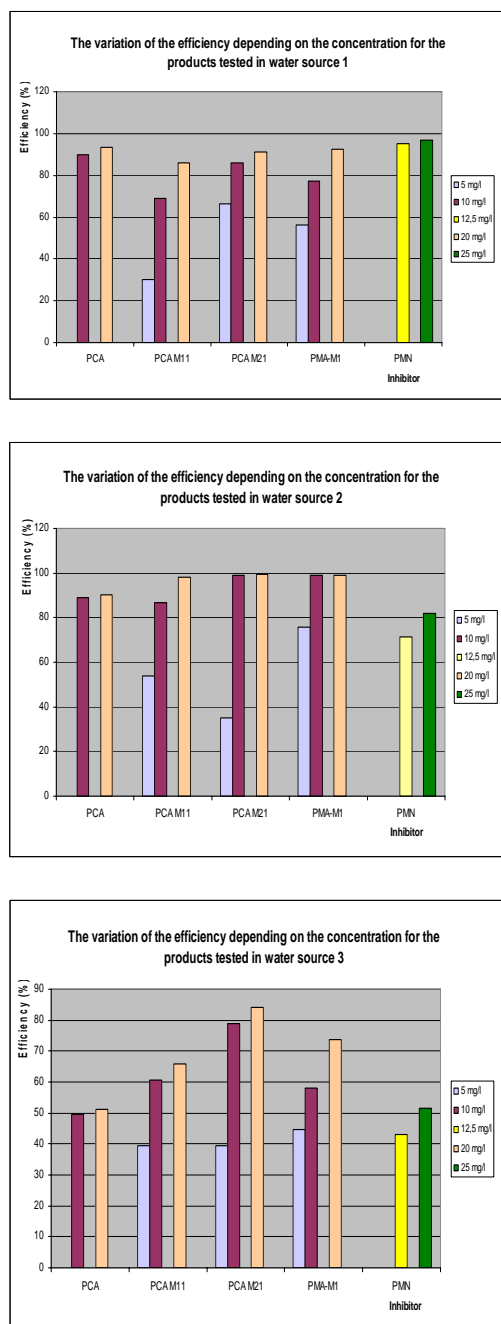


Fig. 2 Mapping antiscaling efficiency of the new inhibitors tested in the three sources of water

III. RESULTS AND DISCUSSION

Some conclusions concerning the antiscaling efficiency which may be concluded from the results presented in Table II and Fig. 2 are the following:

- ✦ according to the experimental data it is evident that the obtained results for source 3 of water are the poorest results concerning the antiscaling efficiency for the new elaborated inhibitors; efficiency more than 80% we have obtained only with the PCA M21 product 20 mg/L

- ✦ the PCA product has given the best antiscaling efficiencies for water from source 1
- ✦ the PCA-M11 and PMA-M1 products (volumetric mixture 1:1 with PBTC) have the best results for water from source 2
- ✦ the PMN product has given the best efficiency for water from source 1
- ✦ for water from source 1 we have obtained the most favorable efficiency (relation efficiency/antiscaling product concentration) with:
 - PCA - 10 mg/L
 - PCA-M11 - 20 mg/L
 - PCA-M21 - 10 mg/L
 - PMA-M11 - 20 mg/L
 - PMN - 12.5 mg/L
- ✦ for water from source 2 we have obtained the most favorable efficiency (relation efficiency/antiscaling product concentration) with:
 - PCA - 10 mg/L
 - PCA-M11 - 10 mg/L
 - PCA-M21 - 10 mg/L
 - PMA-M11 - 10 mg/L
 - PMN - 25 mg/L
- ✦ it is important to notice that due to near results concerning to antiscaling efficiency for 10 mg/L and 20 mg/L concentration of inhibitors, it is recommended to use only 10 mg/L dose because for 3-5% higher efficiency it is not justified to double the inhibitor concentration for industrial applications.

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