Study of maleic anhydride based water treatment agents

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Abstract—The research results of maleic anhydride water treatment agents in the past years were summarized and analyzed, which provided reference for further research and preparation of environmental protection water treatment agents. A binary copolymer product with excellent scale inhibition and dispersion properties was synthesized using maleic anhydride and sodium allyl sulfonate as monomers. The product was characterized and its properties were investigated. It was concluded that the product has excellent scale inhibition and dispersion performance and good biodegradability. The product is an environmentally friendly water treatment agent.

1. Introduction

Almost all industrial enterprises (such as petrochemical, pharmaceutical, chemical fiber, metallurgy, electric power, etc.) tend to generate a lot of heat in the production process, which increases the temperature of production equipment or products and must be cooled in time. Otherwise, the normal operation of production and product quality will be affected [1-3]. In the industry, water is often used as a cooling medium. After the cooling water passes through the heat exchange equipment, the equipment or products are cooled. After the temperature rises, the water is cooled by a cooling tower and then recycled. When the cooling water is recycled, with the evaporation of water, various inorganic salt ions in the water are continuously concentrated, and the concentration of scaling ions increases. The salts in the water exceed their saturated solubility and crystallize out, resulting in scaling phenomena, such as calcium, calcium Magnesium carbonate, sulfate, silicate and phosphate, etc. When it is not serious, it will affect the heat exchange effect and increase energy consumption, and when it is serious, it will block the pipeline and cause an accident [4-5]. Therefore, in the circulating cooling water system, a solution must be selected to solve or improve the above problems.

At present, in the field of circulating water treatment, water treatment agents are generally used to alleviate the scaling phenomenon of water systems. Water treatment agent is a necessary chemical agent in the process of industrial water, domestic water and wastewater treatment. By using these chemicals, the water can meet certain quality requirements.

2. Research progress of polymaleic anhydride

Maleic anhydride (MA) is an important monomer for the synthesis of corrosion and scale inhibitors. The carboxylic acid group in its molecule makes it have excellent negative charge dispersion properties and the ability to complex with other ions. Its molecule does not contain phosphorus and Nitrogen, which avoids the eutrophication of water bodies caused by a large amount of phosphorus and nitrogen enrichment [6-7].

Hydrolyzed polymaleic anhydride (HPMA) is a water-soluble and phosphorus-free high-efficiency scale inhibitor and dispersant. In the early 1970s, it was successfully developed by the Israeli company Chemed, and was first industrialized by the Swiss Ciba-Geigy company as a corrosion and scale inhibitor for cooling water treatment, and then used in seawater desalination and boiler water treatment. In the 1980s, the application was expanded to the fields of detergent and oil field water treatment.

In recent years, many scholars at home and abroad have studied the copolymers of maleic anhydride, and the main achievements are as follows.

Guo Zhenliang et al [8] studied the scale inhibition properties of hydrolyzed polymaleic anhydride under different synthesis conditions. The results showed that when the dosage of HPMA was 12mg/L, the scale inhibition performance of HPMA synthesized by different dosages of catalysts and telomers was different. With the dosage of 1.5% sodium tungstate as the catalyst, the products prepared had different effects on calcium carbonate. The scale inhibition and dispersion performance reached the maximum value.

Ma Ruiting et al [9] studied the corrosion inhibition...
properties of hydrolyzed polymaleic anhydride (HPMA). The results showed that the corrosion inhibitor first increased and then decreased with the increase of HPMA dosage. The best corrosion inhibition effect was 69.3% when the concentration of HPMA was 5.1 mg/L and the concentration of penetrant was 0.5 rag/L.

It can be seen from the research of the above scholars that polymaleic anhydride has certain scale and corrosion inhibition properties, and has a little development prospect.

3. Properties of copolymers of maleic anhydride and other monomers

Copolymers formed by the copolymerization of maleic acid (anhydride) and other different kinds of organic monomers[10], which contain a large number of carboxylic acid groups in the molecule make it more effective in the scale inhibition performance of calcium carbonate and calcium sulfate, outstanding, and its thermal stability is also relatively good [11-13].

Zhao Xiaofei et al[14] synthesized a high temperature resistant water-based drilling fluid viscosity reducer called maleic anhydride/sodium propylene sulfonate/2-acrylamido-methylpropanesulfonic acid (MA/ SAS/AMPS) terpolymer. The optimal reaction conditions of the copolymer were obtained, and its properties were studied, which proved that the copolymer can meet the requirements of viscosity reduction in high temperature deep wells and complex drilling fluids.

Zhu Shengli et al[15] synthesized a copolymer scale inhibitor with maleic anhydride, acrylic acid and ethylene acetate containing ester groups as raw materials, in which water was the solution, ammonium persulfate was selected as the initiator, and isocyanuric acid was selected as the chain transfer agent. The experimental results showed that the copolymer had excellent scale inhibition and dispersibility, and it was economical and environmentally friendly. The equation for the polymerisation reaction is as follows.

\[
\begin{align*}
\text{MA/SAS} & = m\text{CH} + n\text{CH}_2\text{CH}_2 + \text{SO}_3\text{H} + \text{M} + \text{H}_2\text{O} \\
\text{MA/SAS} & = m\text{CH} + n\text{CH}_2\text{CH}_2 + \text{SO}_3\text{H} + \text{M} + \text{H}_2\text{O}
\end{align*}
\]

The authors themselves have also selected sodium allyl sulfonate (SAS) and maleic anhydride to synthesise the MA/SAS copolymer and investigated the conditions for the synthesis of the copolymer, resulting in a two-member copolymer with excellent properties. The products were characterised using both infrared spectroscopy and elemental analysis, and the results are shown in Figure 1 and Table 1, leading to the conclusion that the products were obtained as expected from the binary copolymers. The scale inhibition and dispersion properties of the copolymer were investigated using static experimental methods and the results are shown in Figures 2 and 3, which indicate excellent scale inhibition and dispersion properties. The biodegradation curve of the copolymer is shown in Figure 4, indicating that it is an easily biodegradable substance, degrading 63% after 28d.

The equation for the polymerisation reaction of MA/SAS copolymer is as follows.

\[
\text{MA/SAS}
\]

**Table 1**: Data of Elemental Analysis of MA/SAS Polymer

<table>
<thead>
<tr>
<th>Element</th>
<th>Theoretical value</th>
<th>Actual value</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>33.18</td>
<td>32.76</td>
</tr>
<tr>
<td>H</td>
<td>3.46</td>
<td>3.50</td>
</tr>
<tr>
<td>S</td>
<td>11.10</td>
<td>11.35</td>
</tr>
</tbody>
</table>

**Fig. 1**: Infrared spectra of MA/SAS copolymer.

**Fig. 2**: The scale inhibition performance of MA/SAS copolymer on calcium carbonate.
4. Conclusion

Due to the anhydride and carbon-carbon double bonds contained on the maleic anhydride molecule, it has a strong reactivity. This allows the maleic anhydride to be easily polymerised with other monomers to obtain modified products. The presence of different groups gives it excellent scale and corrosion inhibition properties.

The above scholars had synthesized polymaleic anhydride and copolymers formed by the polymerization of maleic anhydride and other monomers, studied their properties, and made a preliminary exploration of their mechanism. The experimental results showed that the performance of maleic acid water treatment agent was very prominent. The introduction of various groups made the product properties have different emphases, and various synthesis methods have their advantages.

In the future, we will continue to strengthen the research of maleic acid water treatment agent on the basis of previous scholars’ research. Further select appropriate monomers and maleic anhydride for copolymerization, improve the synthesis method and synthesis process, and hope to develop a moderately priced water treatment agent that can be widely used in many fields and has excellent performance. It is necessary to further strengthen theoretical research in the future, and strive to develop scale inhibitors that adapt to different water quality conditions and meet environmental protection requirements.

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References

13. Song Shaofu, Lv Yutao. Research progress of green water treatment agent polyepoxysuccinic acid [J]. Chemical Technology and Development, 2019,