Study on the synthesis and scale inhibition performance of phosphate free environmental protection type poly epoxy succinic acid

Huang Changshan[1, a *], Xu Huiwu [2,b], Chen min[3,c], Zhang min[4,d], Wu Jinying[5,e]

[1,2,3,4,5] Energy Research Institute of Henan Academy of Sciences Co. Ltd., Zhengzhou, 450008, China

[a,b,c,d,e]13937140170@163.com

Keywords: Environmental protection, Poly epoxy succinic acid, Synthesis, Scale inhibition performance.

Abstract. Using maleic anhydride as raw material, sodium tungstate as catalyst, hydrogen peroxide as oxidizing agent, calcium hydroxide as initiator, the synthesis conditions of the best scale inhibition performance of poly epoxy succinic acid were studied by using the method of polymerization: maleic anhydride dosage was 9.8g, the catalyst sodium tungstate amount used is 0.33g, the cyclization response pH value is 4, the initiator calcium hydroxide joins the quantity is 0.5g , polymerization temperature 82˚C, polymerization time 2h. The scale inhibition performance of the poly epoxy succinic acid was evaluated by atomic absorption spectrophotometry: When gathers the poly epoxy succinic acid joins the quantity is 8mg/L, the best effect of the scale inhibition rate of barium sulfate is 98%; When gathers the poly epoxy succinic acid joins the quantity is 40mg/L, the best effect of the scale inhibition rate of strontium sulfate is 90.4%.

Introduction

Phosphorus free environment-friendly water treatment agent has been recognized as the development direction of twenty-first Century water treatment agent [1-2]. Poly epoxy succinic acid was twentieth Century 90's USA Betz lab first developed a non phosphorus nitrogen free "green" water treatment agent [3], Japan and other countries have begun to polye poxy succinic acid and its derivatives were studied by [4].

Research shows that, poly epoxy succinic acid has good synergistic effect, is a kind of low phosphorus scale inhibitor [5-7] or non phosphorus scale and good effect, is a promising inhibitor. The domestic study on poly epoxy succinic acid in the lab, the production process is not stable, it is difficult to obtain the wide application of [8-10]. Therefore, this paper using maleic anhydride as raw material, sodium tungstate as catalyst, hydrogen peroxide as oxidizing agent, calcium hydroxide as initiator, poly epoxy succinic acid by hydrolysis, oxidation, polymerization, ring acidification method, and the influence factors on product performance of scale inhibition was investigated experimentally.

Experiments

Reagents. Maleic anhydride, 30% hydrogen peroxide, sodium hydroxide, calcium hydroxide, sodium tungstate, sodium chloride, sodium sulfate, barium chloride, strontium chloride, anhydrous ethanol, hydrochloric acid, all the reagents were analytical pure grade reagent.

Instruments. 501BS type super constant temperature water bath; JB90-D type strong electric mixer; 402 type vacuum drying box; WH-1 type SR hollow cathode lamp; WH-1 type barium hollow cathode lamp; LAB-200 type fully automatic atomic absorption spectrophotometer.

Experimental methods. 9.8g of maleic anhydride and 18ml deionized water were added to the beaker, stirring to dissolve, pour in three mouth flask. Through the constant pressure drop funnel drop add a certain amount of 50% sodium hydroxide solution, when the bath temperature rose to 60˚C, adds the catalyst sodium tungstate and within 30min uniform droplets with a certain amount of mass fraction as 30% hydrogen peroxide oxidation agent, keep the temperature of water bath at 60˚C, polymerization reaction 2h after, with 50% sodium hydroxide solution adjusting the pH value in 4,

heating, when the rose to a certain temperature, two batches of the canucks initiator calcium hydroxide, temperature is kept constant, a period of reaction, the final product was poly epoxy succinic acid.

Scale inhibition performance evaluation. According to the oil and gas industry standards SY/T 5673-93 " Anti scaling agent performance evaluation method for oilfield ", scale inhibition performance of synthetic product, scale object for barium sulfate and strontium sulfate.

Results and discussion

Effect of amount of catalyst on the product scale inhibition rate. Maleic anhydride was 9.8g, adjust pH value with 50% sodium hydroxide solution, hydrolysis pH was 6~7, cyclization temperature was 60˚C, cyclization pH was 4, cyclization time was 2h, initiator dosage was 0.5g, polymerization time was 2h, polymerization temperature was 82˚C, poly epoxy succinic acid dosage was 8mg/L. Effect of catalyst amount on the product of $BaS0_4$ scale inhibition performance, see Fig.1.

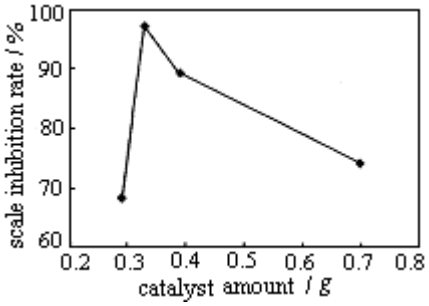

Fig.1 The influence of catalyst amount on the product scale inhibition rate

The catalyst effect of epoxy succinic acid sodium (or epoxy succinic acid sodium hydrogen) yield, which has a certain relation with the nature of the catalyst, the catalyst concentration is low, the effect is not obvious, the resulting product is mainly epoxy succinic acid sodium salt; catalyst concentration is high, then the by-products of tartaric acid, We can see from Fig.1, when the amount of catalyst was 0.33 g, product has good scale inhibition rate.

Effect of cyclic pH on the scale inhibition rate of the product. Maleic anhydride was 9.8g, adjust pH value with 50% sodium hydroxide solution, hydrolysis pH was 6~7, cyclization temperature was 60˚C, cyclization time was 2h, catalyst was 0.33g , initiator dosage was 0.5g, polymerization time was 2h, polymerization temperature was 82˚C, poly epoxy succinic acid dosage was 8mg/L. Cyclization of effect of pH on the product of $BaS0_4$ scale inhibition performance, see Fig.2.

In acid solution, the generation of intermediate product of epoxy succinate sodium prone to side reaction and hydrogen ion, hydrolysis of sodium tartrate; the increase of pH solution is alkaline, and can accelerate the decomposition of hydrogen peroxide, to reduce hydrogen peroxide oxidation ability, maleic acid sodium can not fully epoxidation, leading to reduced, the intermediate product of epoxy sodium succinate yield concentration to reduce, reduce the effective content of poly epoxy succinic acid in the end product, weakening the scale inhibition performance of product. We can see from Fig.2, when the ring pH was 4, the product has good scale inhibition rate.

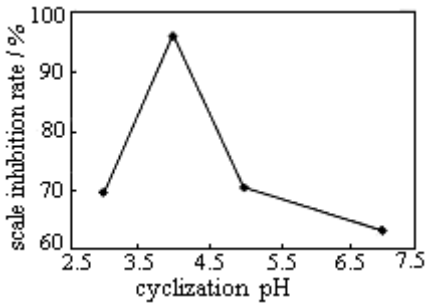

Fig. 2 The influence of cyclization pH on the product scale inhibition rate

Effects of initiator concentration on scale inhibition rate of the product. Maleic anhydride was 9.8g, adjust pH value with 50% sodium hydroxide solution, hydrolysis pH was 6~7, cyclization temperature was 60˚C, cyclization time was 2h, cyclization pH was 4, catalyst was 0.33g, polymerization time was 2h, polymerization temperature was 82˚C, poly epoxy succinic acid dosage was 8mg/L, influence of initiator dosage on product resistance $BaS0_4$ scale properties, see Fig.3.

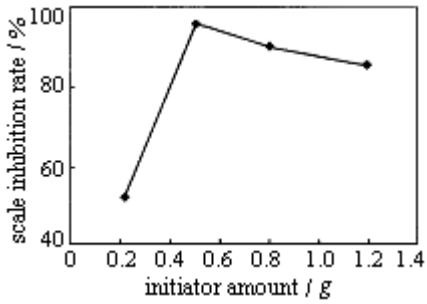

Fig. 3 The influence of initiator amount on the product scale inhibition rate

Initiator dosage has great impact on the degree of polymerization, i.e. that cause a quantity of agent is too small, the synthesis of polyepoxysuccinic acid of high degree of polymerization; initiator dosage too much smaller degree of polymerization, the synthesis of polyepoxysuccinic acid, poly epoxy succinic acid polymerization of sodium is too large or too small, the scale inhibition performance are poor. We can see from Fig.3, initiator dosage was 0.5 g, the product has good scale inhibition rate.

Effect of polymerization temperature on the scale inhibition rate of the product. Maleic anhydride was 9.8g, 50% sodium hydroxide solution adjust pH, hydrolysis pH value 6~7, cyclization temperature was 60˚C, cyclization time was 2h, cyclization pH was 4, catalyst was 0.33g , initiator dosage was 0.5g, polymerization time was 2h, poly epoxy succinic acid dosage was 8mg/L. The influence of temperature on the product of $BaS0_4$ scale inhibition performance of polymerization, see Fig.4.

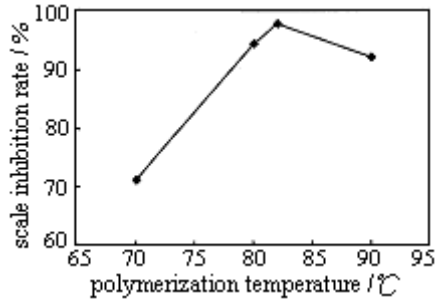

Fig. 4 The influence of polymerization temperature on the product inhibition rate

At low temperature, the polymerization reaction is slower, the strengthening of the hydrolysis reaction of epoxy monomer sodium succinate, monomer polymerization velocity greater than the velocity of hydrolysis; with the increase of temperature, initiator decomposition rate agent to speed up, the degree of polymerization increases, the relative molecular weight of the product increased gradually, the scale inhibition performance to achieve the best; when the temperature is greater than 82˚C poly epoxy succinic acid sodium, high degree of polymerization, the relative molecular weight of the product may be more than with relative molecular weight of the best scale inhibition performance of scale inhibition effect, resulting in decreased. We can see from Fig.4, the polymerization temperature 82˚C is appropriate.

The influence of polymerization time on the product scale inhibition rate. Maleic anhydride was 9.8g, 50% sodium hydroxide solution adjust pH, hydrolysis pH value 6~7, cyclization temperature was 60 ˚C, cyclization time 2h, cyclization pH was 4, catalyst was 0.33g, initiator dosage was 0.5g, polymerization temperature was 82˚C, poly epoxy succinic acid dosage was 8mg/L. The polymerization time effect on the product of $BaS0_4$ scale inhibition performance, see Fig.5.

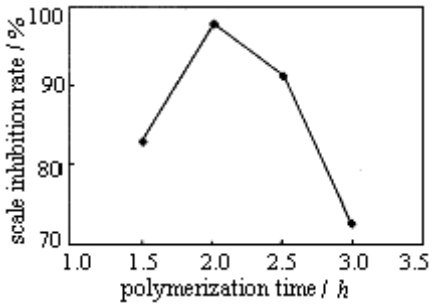

Fig. 5 The influence of polymerization time on the product scale inhibition rate

Time is too short, the product of polymerization degree is too small; the time is too long, polymerization of the products through the large. These two conditions will affect the product of relative molecular weight, thus affecting the scale inhibition effect. We can see from Fig.5, the polymerization time 2h is appropriate.

To sum up, the best technology for maleic anhydride was 9.8g , 50% sodium hydroxide solution adjust pH, hydrolysis pH was 6~7, catalyst was 0.33g, cyclization temperature was 60˚C, cyclization pH was 4, cyclization time was 2h, initiator dosage was 0.5g, polymerization time was 2h, polymerization temperature was 82˚C.

Scale inhibition performance evaluation. According to the oil and gas industry standards SY/T 5673-93 " Anti scaling agent performance evaluation method for oilfield ", scale inhibition performance of synthetic product, scale object for barium sulfate and strontium sulfate. barium, strontium, which ion concentrations were determined by atomic absorption spectrophotometer, the working parameters see Table 1.

Table 1 The operation parameters of atomic absorption spectrophotometer

Determination	Light source	Wavelength (nm)	Flame
Ba	Ba cathode lamp	553.5	Acetylene – air
Sr	Sr cathode lamp	461.5	Acetylene - air

In the following conditions of synthetic products were determined, hydrolysis pH was 6, the amount of catalyst was 0.33g, hydrogen peroxide dosage was 12mL, cyclization pH was 4, cyclization temperature was 60˚C, cyclization time was 2h, initiator dosage was 0.5g, polymerization temperature was 82˚C, polymerization time was 2h. The poly epoxy succinic acid dosage on the effect of scale inhibition rate is shown in Table 2, Table 3.

Table 2 The relationship between dosage of poly epoxy succinic acid and scale inhibition rate (barium sulfate)

Poly epoxy succinic acid amount (mg .L^{-1})	Scale inhibition rate (%)
2	7.1
5	35.6
8	98.0
15	100
20	100

We can see from table 2, when poly epoxy succinic acid added 8 mg/L, the barium sulfate scale inhibition rate can reach 98%; the adding amount 15 mg/L, scale inhibition rate reached 100%. In view of this, poly epoxy succinic acid has good scale inhibition effect on barium sulfate.

Table 3 The relationship between dosage of poly epoxy succinic acid and scale inhibition rate (strontium sulfate)

Poly epoxy succinic acid amount (mg .L^{-1})	Scale inhibition rate (%)
10	30.5
20	55.9
30	81.1
40	90.4
50	98.0

We can see from table 3, the poly epoxy succinic acid synthesis in this experiment, the effect of strontium sulfate scale inhibition than barium sulfate scale inhibition effect slightly worse. Because in the experimental result and the evaluation criteria the solution configuration method has relates greatly, dosage relations may make the performance of scale inhibition of poly epoxy succinic acid is restricted to a certain extent.

Conclusions

Using maleic anhydride as raw material, sodium tungstate as catalyst, hydrogen peroxide as oxidizing agent, calcium hydroxide as initiator, the synthesis conditions of the best scale inhibition performance of polyepoxy succinic acid were studied by using the method of polymerization: maleic anhydride dosage was 9.8g, hydrolysis pH value 6~7, the catalyst sodium tungstate amount used was 0.33g, the cyclization response pH value was 4, the initiator calcium hydroxide joins the quantity was 0.5g , polymerization temperature was 82˚C, polymerization time was 2h.

The scale inhibition performance of the epoxy succinic acid was evaluated by atomic absorption spectrophotometry: When gathers the epoxy succinic acid joins the quantity is 8mg/L, the best effect of the scale inhibition rate of barium sulfate was 98%; When gathers the epoxy succinic acid joins the quantity was 40mg/L, the best effect of the scale inhibition rate of strontium sulfate was 90.4%. The results prove that poly epoxy succinic acid has a unique scale inhibition effect on barium sulfate scale, and the amount of use is lower.

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