Study on Synthetic Technology of Sulfonated Acetone Formaldehyde Polycondensate

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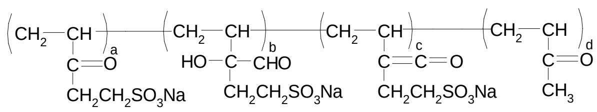
Keywords: Sulfonated Acetone Formaldehyde Polycondensate, Synthetic Technology, Formaldehyde, Additive Method

Abstract. On the basis of the study of the synthetic technology of sulfonated acetone formaldehyde polycondensate, the paper analyzes the polycondensate's synthetic mechanism and advances the three-stage formaldehyde additive technology.

Introduction

Sulfonated acetone-formaldehyde polycondensate is an excellent oil well cement dispersant[1]. Its synthesis mainly makes use of the condensation reaction of aldehyde ketone under the catalysis of alkali and its carboxyl α phase sulfuric methylate reaction where sulfonic group is used to control molecular weight and water-solubility, and to control the condensation and sulfonating degree by adjusting the ratio of aldehyde ketone and sulfonating agent so that the molecular structure with a high water-reducing effect and a fine slump retention is achieved. The molecular structure is as follows[2]:



Based on the molecular structure of sulfonated acetone formaldehyde polycondensate the mechanism of its synthesis is analyzed and its sysnthetic technology is studied here.

Analysis

At present, the raw materials of sulfonated acetone formaldehyde polycondensate are mainly acetone, formaldehyde, Na_2SO_3, $Na_2S_2O_5$ and catalysts. The raw materials show that in the synthetic process, there are probably the following 6 kinds of reactions, including 12 equations:

Hydrolyzing reaction.

Reaction（1）: sulphite's hydrolyzing

$$Na_2SO_3 + H_2O \longrightarrow NaOH + NaHSO_3 \quad (1)$$

Reaction（2）: pyrosulfite's hydrolyzing

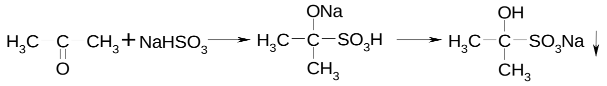
$$Na_2S_2O_5 + H_2O \longrightarrow 2\,NaHSO_3 \quad (2)$$

Nucleophilic addition reaction[3-4].

Reaction（3）: addition of formaldehyde and sodium bisulfite

$$H-\underset{\underset{O}{\|}}{C}-H + NaHSO_3 \longrightarrow HO-CH_2-SO_3Na \downarrow \quad (3)$$

Reaction（4）: addition of acetone and sodium bisulfite



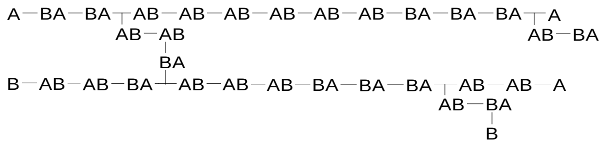
(4)

In Reactions（3）and（4）, the white deposit which is not soluble in supersaturation $NaHSO_3$ is produced. In the reactions, the agent's nucleophilic center is not oxygenic atom, but sulphuric atom: the additional product is not sulfuric acid ester, but α-hydroxy sulfonic acid sodium. This product is water-soluble, but not soluble in saturation $NaHSO_3$ liquid, so as to separate out in deposition. When we made the synthetic test, we could see the white deposit appearing obviously, which proves this reaction's existence. But the white deposit would disappear after a period of time, because with the existence of acid or alkali, after water is added to dilute, the product is again to decompose into the previous aldehyde or ketone[5], therefore it will not affect the composition of the water-reducing agent. Besides, Reaction (4) is adverse to the synthesis of water reducing agent, and should be controlled,so the addition of acetone in the hydrolysis stage is not advocated.

Cross linking reaction.

The gradual polymerization of two monomers（A-A and B-B）or the gradual polymerization of one monomer（A-B）can only produce the linear polymer. When one or more monomers have over two functionalities, the reaction result is: at first, the fork chain is formed, and after the further reaction and crossing linking, the three-dimension polymer appears. The reaction in which the bonding between big molecular links produces cross-linking polymers is called the cross linking reaction. The change in structure caused by that reaction is as follows:

Reaction（5）:



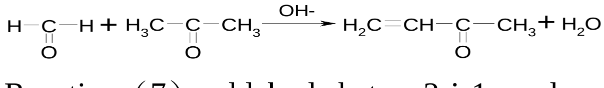
(5)

When the polyfunctional group system is polymerized to some extent, cross-linking begins, viscosity increases abruptly, bubbles are hard to rise, the gel appears, and the degree this time is called gelling point[6]. The cross-linking reaction is very important to the synthesis of high polymers like rubber, but very harmful to hi-efficient water-reducing agents, causing them to have no dispersivity. In the above nucleophilic addition reactions, after acetone and sodium bisulfite are added, the product will have 4 functionalities, providing the condition for the production of the cross-linking net structure. According to the theory of functionality, if in this synthetic process, the amount of sodium sulfite is reduced and PH value adjusted, the reaction degree can be controlled and the gelling point is improved so as to prevent the gelling from appearing. Therefore, in the synthetic process, the amount of sodium sulfite must be controlled within a certain range[1].

Aldol condensation reaction[2-8].

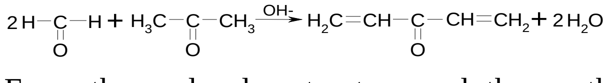
Under the condition of alkali, with the existence of formaldehyde and acetone, because acetone has 4α-H, it can undertake the crossed aldol condensation reaction with formaldehyde and different products are made for different material ratios.

Reaction（6）: aldehyde ketone1∶1 condensation



(6)

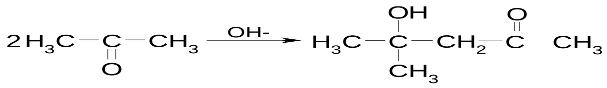
Reaction（7）: aldehyde ketone2∶1 condensation



(7)

From the molecular structure and the synthetic mechanism of sulfonated ketone aldehyde polycondensates, aldol condensation reaction is of much importance for it is the key to the synthesis, in which Reaction（6）and its products should be strengthened, while Reaction（7）and its products should be restrained. Therefore, when the synthesis is conducted, it is better to use aldehyde ketone1∶1 condensation, avoiding using too much formaldehyde. In addition, from the chemical quality of aldehyde and ketone, there should be the self condensation of aldehyde and ketone besides aldol crossing condensation reaction. But because formaldehyde has no α-H and cannot self-condensate, it is only possible to have acetone's self-condensation.

Reaction（8）: acetone's self-condensation

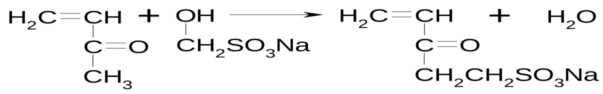


(8)

The self-condensation of acetone is not beneficial to the synthesis of water-reducing agent, which should be controlled. But the balance of Reaction（8）leans to the reactant and there is a low producing rate of the condensate（only about 5%）, without much influence. Meanwhile, when test or production is conducted, it can be considered that acetone is slowly dripped into the liquid so as to reduce the possibility of the self-condensation from the experimental way.

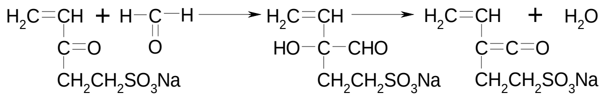
Polymerization reaction[2-8].

Reaction（9）:



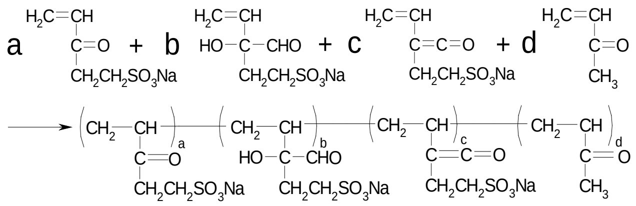
(9)

Reaction（10）:



(10)

Reaction（11）:



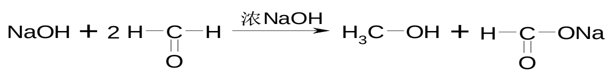
(11)

The above three reactions can be controlled by temperature and reaction time. What should be pointed out is that to get the pectinated multipolymer, Reaction（10）is very important. Therefore, in the stage of polymerization reaction, there should be another formaldehyde-adding technology.

Cannizzaro reaction[9].

In the thick alkali liquid, aldehyde without α-H atoms may have the dismutation reaction, part of which is oxidized into carboxylic acid and the other part of which is returned into alcohol. This reaction was discovered by S. Cannizzaro（1826-1910）in 1853, so it is called Cannizzaro reaction, also called dismutation reaction.

Reaction（12）: Cannizzaro reaction



(12)

In the synthetic test, acid flavor is smelled in some synthetic reactions, showing that organic acid is produced and there is Cannizzaro reaction. Although this reaction is unavoidable, the reaction degree is small and has little effect on the synthesis.

Conclusion

According to the above 12 reaction equations and the theoretic analysis, it is known that to get the polymer with a certain amount of SO_3M group, Reactions（3）、（4）、（5）、（6）、（7）、（8）、（9）、（10）and（11）must be well controlled, and the reaction order should be Reaction（3）is the first, then Reaction（6）, then Reactions（9）and（10）, Reaction（11）is the last; and at the same time, Reactions（4）,（5）,（7）and（8）should be prevented from happening. Analyzed from the above, the three-stage formaldehyde-adding technology should be used to synthesize the sulfonated acetone formaldehyde polycondensate.

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