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Synthesis and application of new fluorosilicon surfactants

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ABSTRACT
Based on the research of organofluorine surfactant and organosilicon surfactant, a new type of surfactant synthesized by combining the excellent properties of the two is a new type of surfactant, which has a variety of good characteristics such as good wettability, superspreadability, high and low temperature resistance, etc., and has a promoting effect on the actual production and application. This article summarizes the current research on the characteristics of organosilicon and organofluorine surfactants, the synthesis method of fluorosilicon surfactants, and their practical production applications.

KEYWORDS
fluorosilicon surfactant; synthesis preparation; Practical application

1 Introduction

Surfactants are widely used and have the property that the addition of small amounts can significantly reduce the surface tension of the solution. According to the type of hydrophobic group, surfactants can be divided into five categories: hydrocarbon surfactants, organofluorine surfactants (hydrophobic groups with fluorinated or partially fluorine carbon and fluorine chains), silicone surfactants (with polydimethylsilane as the hydrophobic backbone), organoboron surfactants, and fluorosilicon surfactants[1](hydrophobic groups contain both F and Si elements)[2].

Among them, the chemical structure of organofluorine surfactant contains short C-F bonds, high bond energy, good thermal and chemical stability, low surface tension, high surface activity, excellent hydrophobic and oleophobicity, corrosion resistance, oxidation resistance, high temperature resistance and other excellent properties, which can be practically applied in oilfield, chemical industry, biomedicine and other fields. However, it also has poor low temperature resistance, and the raw materials such as perfluorooctane sulfonic acid (PFOS) salts, esters and their derivatives used in the synthesis process are persistent in the environment, non-degradable, highly bioaccumulative, toxic, and can migrate with the environment over long distances [3], which cannot fully meet the green environmental protection concept advocated by today's society. Silicone surfactant refers to a class of polysiloxane with Si-O as the main chain (the bond energy of Si-O is significantly higher than that of C-C bond and C-O bond), silicon-carbon ane or silane is the hydrophobic chain, and the silicon-containing high-efficiency special surfactant containing silicon is connected to one or more hydrophilic groups in the main chain or branch chain, which has good wettability, super-spreading, high and low temperature resistance, defoaming and foam stabilization, etc., and can be used in coal mining, pesticides, chemicals, textiles, fire extinguishing agents and other fields. In order to obtain surfactants with more excellent characteristics, the current research will combine the excellent characteristics of organic fluorine and silicone surfactants (containing both F and Si) as the research direction, and promote innovative research to develop surfactants that are more in line with production needs.

2 Synthesis and preparation of fluorosilicon surfactants

Fluorosilicon surfactants are divided into ionic and non-ionic types, and the synthesis methods and actual uses of the two are different. In this paper, three commonly used traditional preparation methods are summarized: silicon hydrogenation method, free radical polymerization method, and polycondensation method.

2.1 Hydrosilicon addition

Hydrosilicon addition reaction is an addition reaction of hydrosilane or hydrosilicone oil containing Si-H bond and fluoroolefin or fluoroalkyl alkenyl ether under certain conditions, which is the most commonly used method for synthesizing fluorosilicon surfactant under mild conditions and high yield.

At present, silicon-hydrogen addition reactions can be divided into the following three main types[4].

（1）The fluorohydrocarbon group and hydrogen-containing silane were used as raw materials for silicon-hydrogen addition reaction, and the fluorosilicon surfactant was further prepared by hydrolysis and polycondensation reaction, as shown in Figure 1-2;

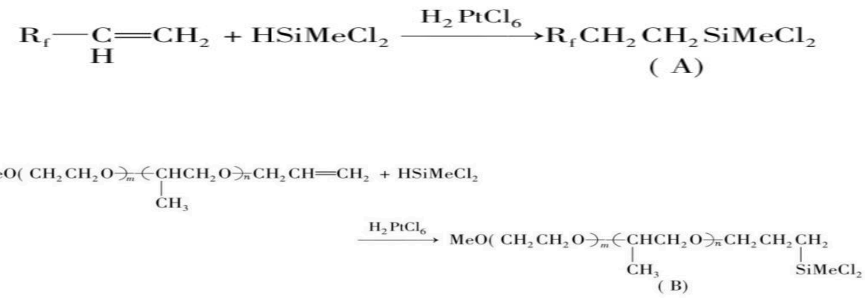

Figure 1 silicon-hydrogen addition reaction

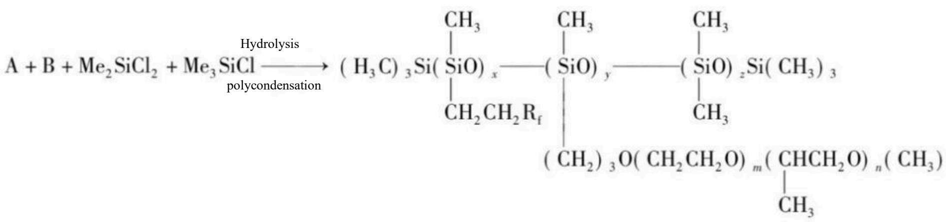

Figure 2 hydrolysis and polycondensation reaction

（2）Fluoroalkyl alkenyl ether and hydrogenated silicone oil are used as raw materials for silicon-hydrogenation reaction, as shown in Figure 3.

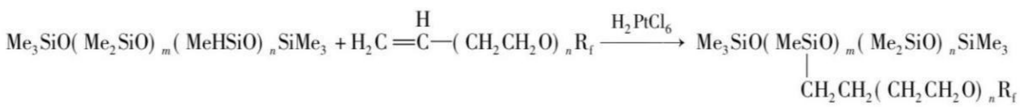

Figure 3 silicon-hydrogenation reaction

（3）Fluorosilicon nonionic surfactants were prepared by hydrosilicon addition reaction of fluorosilicon compounds containing Si-H bonds and polyoxyethylene containing allyl oxide groups, as shown in Figure 4.

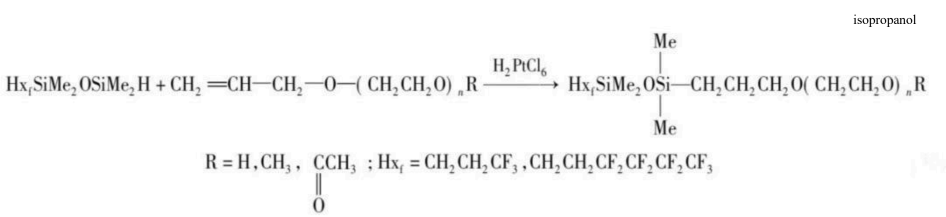

Figure 4 silicon-hydrogenation reaction

(1) Epoxy polyether fluorosilicon surfactant

Zhang Le, Huang Liangxian et al.[5] used α - ω hydrogen-containing fluorinated silicone oil (FPHS) and allyl epoxy polyether as raw materials to prepare epoxy polyether fluorosilicon surfactant (FPES) by silicon hydrogen addition, as shown in Figure 5.

The optimal conditions of the reaction are as follows: the reaction temperature is 80 °C, the reaction time is 3h, n(Si-H):n(C=C)=1:1.075, and the catalyst dosage is 0.005% (when Pt is used as catalyst).

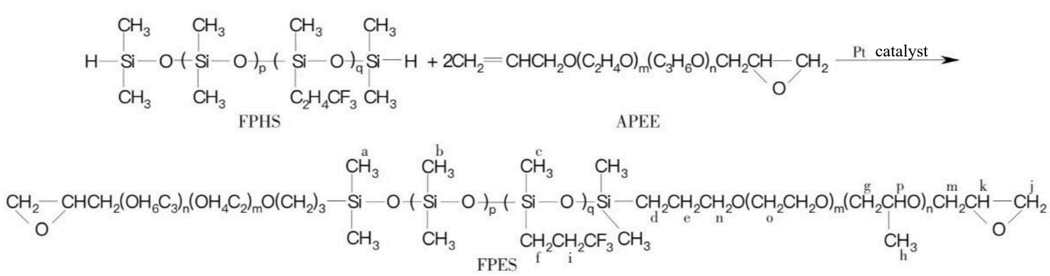

Figure 5 silicon-hydrogenation reaction of FPES

(2) Phosphate-ester fluorosilicon surfactant

Huang Liangxian, Zhang Le et al.[6] used hydrofluorosilicone oil (FPHMS) and allyl hydroxypolyoxyethylene ether (FAE-10), benzene as solvent, and H2PtCl6 as catalyst to prepare intermediate hydroxyl polyether modified fluorosilicone oil (THPEFS) through hydrosilicon addition reaction, and then esterified THPEFS and phosphoric acid to prepare phosphate fluorosilicon surfactant (PFSS).

Step 1: To prepare the intermediate THPEFS

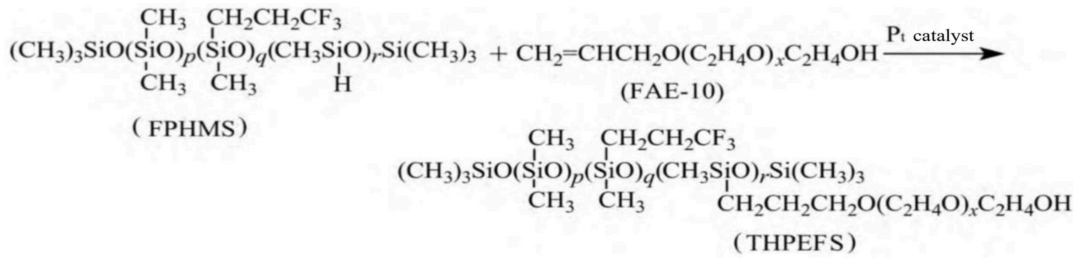

Figure 6 Synthesis of intermediates THPEFS

Step 2: Prepare the PFSS

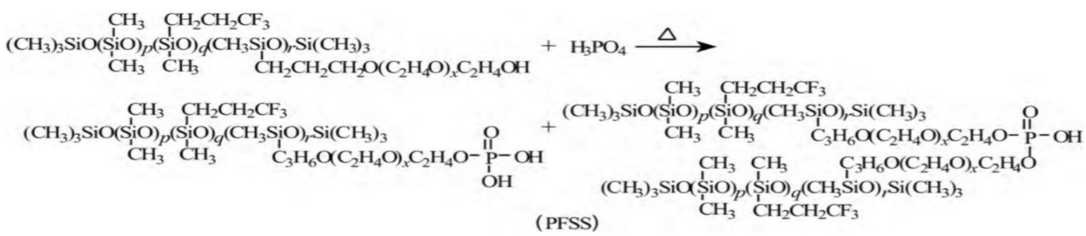

Figure 7 Synthetic PFSS

The optimal conditions for the esterification reaction are as follows: the reaction temperature is 70 °C, the reaction time is 6h, n(THPEFS):n(H_3PO_4)=1:1.1.

(3) Sulfonate fluorosilicon surfactant

Zhang Le, Huang Liangxian et al.[7] used octamethylcyclotetrasiloxane, 1,3,5-trimethyl-1,3,5-tris(3,3,3-trifluoropropyl) cyclotrisiloxane, tetramethyldisiloxane, allyl epoxy polyether and $KHSO_3$ as raw materials to prepare sulfonate-type fluorosilicon surfactant FPESS by ring-opening polymerization, hydrosilicon addition reaction and sulfonation reaction.

Step 1: Preparation of fluorine-containing hydrogenated polysiloxane (FPHS).

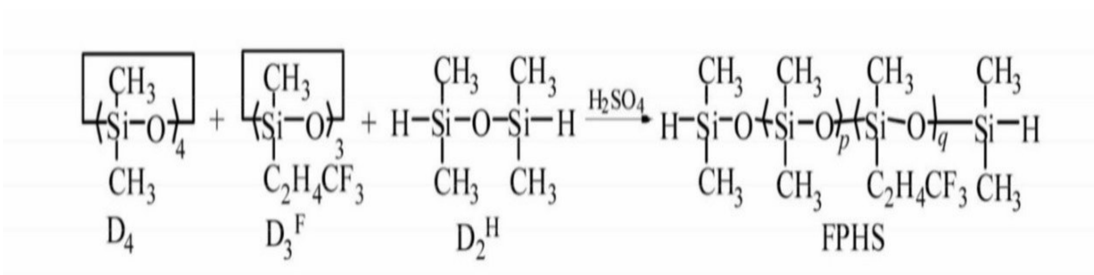

Figure 8 Synthetic FPHS

Step 2: Epoxy polyether modified fluorinated polysiloxane (FPES) is prepared.

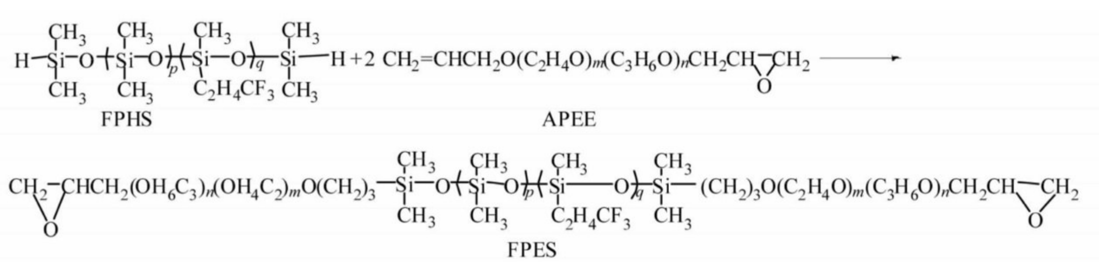

Figure 9 Synthetic FPES

Step 3: To prepare sulfonate fluorosilicon surfactant (FPESS)

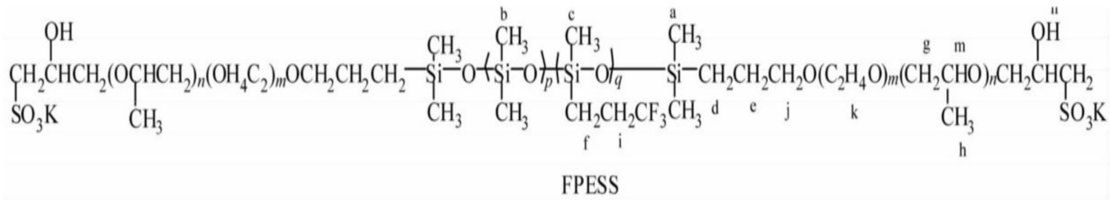

Figure 10 The structural formula of FPESS

The optimal conditions for FPESS sulfonation reaction were as follows: the reaction temperature was 60 °C, the reaction time was 6h, n (epoxy group): n ($KHSO_3$) = 1:1.2.

2.2 Free radical polymerization method

Free radical polymerization is a chemical reaction in which monomer molecules are activated into active free radicals under the action of light, heat, radiation and initiators, initiated by free radicals, and then polymerized with monomers to form polymers. According to the physical state of the reaction system, free radical polymerization can be divided into emulsion polymerization, solution polymerization, bulk polymerization, and supercritical CO2 polymerization[1].

Fluoroalkyl alkene ethers (or fluoroolefins) and silanes containing double bonds were used as raw materials, and the reaction catalyst was further selected according to the reaction conditions[8]. Taking fluoroalkyl olefins and vinyl silanes as raw materials for free radical copolymerization as an example, as shown in Figure 11(a);

Perfluoropolyether diacylperoxide $(R_fCOO)_2$ was used as the initiator, and acrylic acid and vinyl trimethylsilane were used for copolymerization reaction, as shown in Figure 11(b).

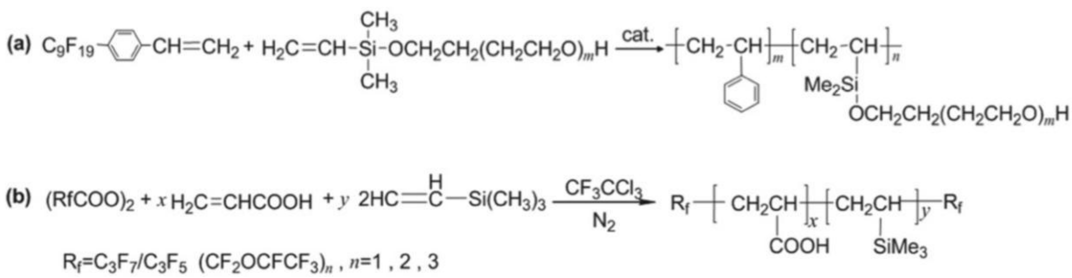

Figure 11 Free radical copolymerization reaction

2.3 Polycondensation method[1]

Polycondensation is a process in which one or several monomer organic compounds containing two or more functional groups are synthesized into polymers and precipitate small molecule by-products (such as water, hydrogen halide and other small molecules). The polycondensation method is significantly different from the previous radical polymerization, and the polymerization mechanism adheres to the condensation reaction mechanism. Due to the defects of the condensation mechanism, the polymer composition prepared by this method is relatively single and unevenly distributed. Boutevin et al.[9] synthesized a modified fluorosilicon polymer with a silicon-oxygen chain as the main chain by polycondensation reaction using dichlorofluorosilane and dihydroxyfluorosilane as monomers and dimethylphenyl chlorosilane as capping agents.

3 Application of fluorosilicon surfactant

As a new research direction, the new fluorosilicon surfactant combines the excellent characteristics of organofluorine and organosilicon surfactants, and shows good wettability, superspreadability, high and low temperature resistance, defoaming and foam stabilization, etc., and has a larger and broader application market.

3.1 Fluorosilicon surfactants – coatings

Fluorosilicon surfactants are generally widely used in the coating industry due to their low surface tension, good stability and good dispersion. Compared with other coatings, the prepared fluorosilicone coating has better antifouling, waterproofing, weather resistance and good chemical stability, and the common application fields are the protective layer of building exterior walls, the antifouling of marine ships and some special protective coatings.

On the exterior walls of buildings, the coatings used often focus on high and low temperature resistance, light resistance, antifouling and other performance aspects. At present, the water-based environmentally friendly fluorosilicone coating[10] is developed by blending and modifying fluorosilicone resin and non-fluorosilicone resin, using nanomaterial application technology and the principle of gradient self-layering, which has achieved the characteristics of super weather resistance and stain resistance, and can realize further innovation and iteration in the application market.

At present, the fouling caused by marine organisms is serious, and the most direct impact is the fouling and damage to the hull of marine ships, so environmental protection, efficient and extensive marine antifouling treatment is very important. Among them, fluorosilicone polymer marine antifouling coating, as a low surface energy antifouling coating, combines the advantages of fluorocarbon resin and silicone resin, and has excellent characteristics such as good mechanical properties and polymer softness, and the prepared fluorosilicone coating has good stability, hydrophobicity, oil repellency, and antifouling ability[11].

3.2 Fluorosilicon surfactant - rubber surface modifier

Rubber is widely used in various fields of production and life, and fluorosilicone surfactants are often widely used as rubber surface modifiers, release agents, antistatic agents, etc. added to rubber, which makes the production of fluorosilicone rubber have high and low temperature resistance, oil resistance, good electrical properties and resilience of silicone rubber, as well as excellent characteristics such as oil resistance, solvent resistance, saturation resistance and other excellent characteristics of fluorine rubber, which are commonly used to produce products that require chemical corrosion resistance, but there are also defects such as poor strength, low surface energy, and difficult processing. Therefore, it is crucial to develop appropriate formulations and processing techniques to improve the performance of rubber compounds[12-13].

3.3 Fluorine silicon surfactant - fire extinguishing agent

The polyfluorinated side group of fluorosilicone defoamer makes it have lower surface energy than methyl silicone oil, and has good thermal stability, chemical resistance and other characteristics. Among them, the fluorine silicon defoamer developed by Soochow University[14] contains 100% defoaming active substances, which can be dispersed into a defoaming unit in the defoaming liquid to achieve excellent defoaming and foaming inhibition capabilities. It has strong defoaming and foam inhibition ability in the temperature range of 0~150 °C, and can be applied to oil phase defoaming when the dosage is between 0.2%~1%.

3.4 Fluorosilicon surfactants - oilfield exploitation

As a non-renewable resource, oil is the backbone of industrial energy and is indispensable for people's daily life and travel. Heavy oil accounts for the majority of the oil, and because of its high viscosity, it often adheres to the rocks during extraction. As an oil displacement agent, fluorosilicon surfactant can significantly reduce its surface tension and have the effect of emulsifying and reducing viscosity. When the surface tension between oil and water decreases, the better the emulsifying ability of crude oil, the easier it is for the oil film to be extracted from the rock, and the more fluid it is, thus improving the recovery rate of crude oil[15].

4 Prospect of fluorosilicon surfactants

Fluorosilicon surfactant combines the excellent characteristics of organofluorine surfactant and organosilicon surfactant, which is a novel and promising research direction, and there is still a lack of further research, synthesis and application of fluorosilicon surfactant in China.

According to the good wettability, superspreadability, high and low temperature resistance, defoaming and foam stability of fluorosilicon surfactant, some technologies have been industrialized, which can be used in coal mining, pesticides, marine antifouling, chemicals, textiles, fire extinguishing agents and other fields. According to the needs of production and life, researchers can study new modified fluorosilicon surfactants, introduce different groups, make the prepared fluorosilicon surfactants have more stable and excellent characteristics, and expand the application of fluorosilicon surfactants.

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