Optimum Synthesis Conditions of High Quality Explosive Emulsifier Sorbitol Monooleate

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Abstract. Sorbitol monooleate (Span80) is an extensively used explosive emulsifier at present. It is a kind of non-ionic surfactant with low molecular weight polyols, which belongs to water-in-oil emulsifier and has good emulsifying performance. The low-quality oleic acid was used as raw material. In order to optimize the synthesis conditions of Span80, the effects of different types of catalyst, reaction time and reaction temperature on the acid value, saponification value and hydroxyl value of Span80 were investigated, and the synthesis conditions of Span80 were optimized. The results showed that 159g sorbitol and 360g oleic acid, with 0.2% Zinc Oxide as catalyst, reacted with 2.5h at 210℃ in vacuum, at this time the acid value, saponification value and hydroxyl value of product Span80 were 5.8mgKOH/g, 154.1mgKOH/g and 207.3mgKOH/g, respectively. This method provided a reference for the synthesis of high quality and low cost emulsifiers, and had important significance for civil emulsion explosive enterprises.

1.Introduction
Emulsifier is closely related to storage stability and explosive properties of emulsion explosive[1-2]. Emulsifiers have been extensively studied by domestic and foreign scholars[3-8]. Among them, sorbitol monooleate (Span80) is widely used as an explosive emulsifier[9-10], which is a low molecular polyl non-ionic surfactant[11] and a water-in-oil emulsifier. It has good emulsifying property[12-13]. Span80 is used to synthesize emulsion explosive without high shear force, which improves the production safety factor[10].

At present, the synthesis method of Span80 is more mature, which is synthesized by the reaction of sorbitol with oleic acid under the action of catalyst[12]. However, how to develop cheap emulsifier with strong emulsifying property and high storage stability is a great significance to civil emulsion explosive enterprises. In this paper, inferior oleic acid was used as raw material to optimize the synthesis conditions of Span80, which could provide reference for the synthesis of high-quality and low-cost emulsifiers.

2.Materials and methods
2.1Experimental materials
Main reagents: sorbitol (purity 70%), Shandong Tianli Pharmaceutical Co., Ltd., oleic acid (purity 60%), Dalian Yindong Chemical Co., Ltd. Sodium hydroxide, sodium bicarbonate, phosphoric acid, sulfuric acid, p-toluenesulfonic acid, zinc oxide, pyridine, anhydrous alcohol, ethyl acetate, perchloric
acid, hydrochloric acid, potassium hydroxide, phenolphthalein.
Main instruments: HH-S digital display constant temperature oil bath, Jintan Jiangnan instrument factory; SHZ-D (III) circulating water vacuum pump, Gongyi Zihua instrument Co., Ltd.

2.2 Synthetic methods
Took a certain amount of sorbitol and catalyst in three flasks, added a proper amount of oleic acid, inserted electric stirring rod into the middle of the flask, inserted a thermometer at one end of the flask, connected the other end to the condensing tube, connected the end of the condensing tube with a tail tube with a vacuum. Then connected the conical bottle, immersed the three flasks in the oil bath pot, start the electric stirrer and the heating device of the oil bath pot, set the temperature as the required reaction temperature, used the medical vacuum pump to vacuum the experimental device, and its vacuum degree needs to be above 0.08MPa. Heated up to the desired temperature and maintain a constant temperature reaction for a period of time. At the end of the reaction, the reaction products in the three flasks were dissolved with a certain amount of anhydrous ethanol. The filtrate was extracted by vacuum filtration and then distilled by vacuum distillation to remove the solvent. The acid value, saponification value and hydroxyl value of the product were determined.

2.3 Impact factor tests
The kinds of catalysts (acid catalyst: phosphoric acid, p-toluene sulfonic acid, sulfuric acid), alkaline catalyst: sodium carbonate, sodium hydroxide, sodium stearate; The effects of reaction temperature and reaction time on the Span80 properties of the synthesized products were investigated. Three parallel trials were conducted in each group.

2.4 Determination of indicators
The Span80 properties of the synthesized products include acid value, saponification value and hydroxyl value. According to the regulations of the National Standard of the people's Republic of China for Food Safety and the Food Additive Sorbitol Anhydride monooleate (GB 13482-2011), the qualified physical and chemical indexes of Span80 are: acid value (mgKOH/g)≤8. The saponification value (mgKOH/g) was 145-160 and the hydroxyl value (mgKOH/g) was 193-210.

The acid value, saponification value and hydroxyl value were determined by the National Standard of the people's Republic of China food additive Sorbitol Anhydride monooleate (Span80)>(GB 13482-2011).

3. Results and discussions
3.1 Effect of type of catalyst
3.1.1 Acid catalyst. At 210 ℃, 159g sorbitol, 360g oleic acid and 0.2wt% acid catalyst were prepared at 210 ℃ for 3 h. The Span80 properties of the synthesized product are shown in Table 1.

| Catalyst                  | Acid value / (mgKOH/g) | Saponification value / (mgKOH/g) | Hydroxyl value / (mgKOH/g) |
|---------------------------|------------------------|----------------------------------|---------------------------|
| Phosphoric acid           | 12.6                   | 166.8                            | 154.7                     |
| P-toluene sulfonic acid   | 10.8                   | 240.5                            | 132.9                     |
| Sulphuric acid            | 9.5                    | 193.7                            | 165.6                     |

Table 1 showed that the acid value and saponification value of the products corresponding to the three acidic catalysts were high and the hydroxyl value was low compared with the qualified physical and chemical indexes of Span80 in the national standard. Therefore, acid catalyst can not be used in
the synthesis of Span80.

3.1.2 Alkaline catalyst. After the reaction of 159 g sorbitol, 360 g oleic acid and 0.2% basic catalyst at 210 °C for 3 h, the Span80 properties of the synthesized product are shown in Table 2.

| Catalyzer            | Acid value/(mgKOH/g) | Saponification value/(mgKOH/g) | Hydroxyl value/(mgKOH/g) |
|----------------------|----------------------|--------------------------------|--------------------------|
| Sodium carbonate     | 8.2                  | 142.8                          | 176.4                    |
| Sodium hydroxide     | 4.3                  | 145.2                          | 213.7                    |
| Sodium stearate      | 52.3                 | 257.4                          | 124.6                    |

Table 2 showed that the saponification value of Span80 was higher and the hydroxyl value was lower when sodium carbonate was used as catalyst in the three basic catalysts. When sodium hydroxide was used as catalyst, the acid value and saponification value of the product reached the national standard, but the hydroxyl value was on the high side. The effect of using sodium stearate as catalyst was not good, the physical and chemical indexes of the synthetic products were not within the scope of national standard, and it was found in the experiment that the synthetic products were almost not dehydrated. Therefore, the alkaline catalyst is not conducive to the synthesis of Span80.

3.1.3 Oxide catalyst. After the reaction of 159 g sorbitol, 360 g oleic acid and 0.2% oxide catalyst at 210 °C for 3 h, the Span80 properties of the synthesized product are shown in Table 3.

| Catalyzer            | Acid value/(mgKOH/g) | Saponification value/(mgKOH/g) | Hydroxyl value/(mgKOH/g) |
|----------------------|----------------------|--------------------------------|--------------------------|
| Magnesium oxide      | 9.6                  | 169.9                          | 210.4                    |
| Zinc oxide           | 5.8                  | 157.1                          | 207.3                    |
| Alumina              | 28.9                 | 178.3                          | 122.7                    |

From Table 3, it can be seen that the acid value, saponification value and hydroxyl value of the products obtained by using magnesium oxide as catalyst were higher than that of the national standard. Using zinc oxide as catalyst, the catalytic effect was ideal, each index was in the range of qualified product index, the acid value of the product was higher, but the hydroxyl value was very low, using alumina as catalyst. Therefore, the synthesis of Span80 with zinc oxide as catalyst is ideal.

3.2 Effect of reaction temperature

The synthesis of sorbitol monooleate is a reversible reaction. According to the principle of reaction kinetics, the influence of temperature on the reaction equilibrium constant is very important, and the reaction kinetic energy is determined by the temperature. The temperature is too low, the reaction kinetic energy is insufficient, and the reaction cannot be carried out. If the temperature is too high, the reaction kinetic energy will be large, the side reaction will increase, so the impurity content is more, and the dehydration speed is fast, which will cause the serious coking of sorbitol and oleic acid, and destroy the raw material molecule and lead to the poor product quality. Therefore, the key to the experiment is to control the reaction temperature.

Under the reaction conditions of 190、200、210、220 and 230 °C for 3 h, the Span80 properties of the synthesized products were shown in figure 1. The reaction of 159 g sorbitol, 360 g oleic acid and 0.2% zinc oxide was carried out at 190、200、210、220 and 230 °C for 3 h, respectively. The properties of the synthetic product Span80 are shown in Figure 1.
From Figure 1, it can be seen that the hydroxyl value of Span80 decreases slowly and the saponification value increases with increasing reaction temperature, which may be the result of conversion of monoester to diester or polyester. And with the increase of reaction temperature, the reaction rate also increases. Therefore, the reaction temperature should be set at 210 ℃. The acid value, saponification value and hydroxyl value of the product obtained at this temperature are within the range of physical and chemical indexes.

**3.3 Effect of reaction time**

Controlling reaction time is another key to the synthesis of high quality sorbitol monooleate. If the reaction time is short and the esterification is incomplete, the acid value of the product is high. When the reaction time is long, the acid value decreases, but the decomposition of ester also increases, and the acid value will rise again[14].

At 210 ℃, 159g sorbitol, 360g oleic acid and 0.2% zinc oxide were reacted at 210 ℃, respectively. The Span80 properties of the synthesized products were shown in Figure 2.

From Figure 2, with the increase of reaction time, the acid value and hydroxyl value of Span80 decreased gradually, and the saponification value increased. This is because the reaction time increases and the esterification rate increases. When the reaction time was 2.5 h, the acid value of the product increased, which may be the result of the increase of ester decomposition amount. Therefore, when the reaction time is 2.5 h, the acid value, saponification value and hydroxyl value of the product accord with the national standard.
4. Conclusion

The optimum conditions for the synthesis of high quality sorbitol monooleate were as follows: sorbitol and oleic acid were fed at 159g and 360g, respectively. Zinc oxide with 0.2% of raw material was used as catalyst, and the reaction was carried out at 210 ℃ for 2.5 h.

Under the optimum synthesis conditions, the acid value, saponification value and hydroxyl value of the product Span80 are 5.8mgKOH/g, 154.1mgKOH/g and 207.3mgKOH/g respectively, which meet the national standard. This method provides a reference for the synthesis of high quality and low cost emulsifiers and is of great significance to civil emulsion explosive enterprises.

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