

A Polyester Modified Organic Silicon Levelling Agent and Its Preparation Method

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Abstract: This Paper Introduces the Preparation and Application of a Polyester Modified Organic Silicon Levelling Agent. through the Chemical Modification of Polyester and Organic Silicon, the Obtained Polyester Modified Organic Silicon Levelling Agent Has Good Performance in High Temperature Resistance. It is Suitable for the Baking Varnish System, and Has Good Levelling Property, Compatibility, and Anti-Shrinkage Ability. the Agent Also Improves the Hand Print Resistance of the Paint Film.

1. Introduction

Levelling Agent is a Commonly Used Coating Additive. According to Different Chemical Structures, Levelling Agents with Surface Control Ability Can Be Divided into Three Categories: Acrylic Acids, Organic Silicon and Fluorocarbon. in the Prior Art, the Method of Preparing Polyester Modified Organic Silicon Levelling Agent is to React Siloxane and Allyl Polycaprolactone At the Presence of Catalyst. This Method is High Cost and Can Produce Serious Pollution; the by-Products Are Difficult to Be Removed from the Target Product. Moreover, the Obtained Organic Silicon Levelling Agents Have Poor Heat Resistance. They Are Not Suitable for High Temperature System; the Performances of Products Are Not Good. in Order to Overcome the Shortcomings of the Existing Technology, It is Necessary to Develop a Product with More Excellent Performances; the New Product Needs to Ensure the Conventional Levelling Performance and Have Better Performances in Temperature Resistance and Compatibility in the Coating System.

2. The Experiment

2.1 Raw Materials

Raw Materials in This Experiment Include Isophthalic Acid, Terephthalic Acid, Stearic Acid, Oleic Acid, Adipic Acid, Phthalic Anhydride, Maleic Anhydride, Trimellitic Anhydride, Neopentyl Glycol, Trimethylolpropane and Polydimethylsiloxane. All Above Reagents Are Industrial Grade.

2.2 Modification Method

The polyester organic silicon levelling agent was prepared by the reaction between the hydroxyl terminated organic silicon oil with structural formula 1 of $\text{HO}[(\text{R}_1)_2\text{SiO}]_n\text{R}_2$ and the carboxyl functional group in the catalyst condition. In the reaction, R1 was one or several mixtures of the methoxyl group, the oxyethyl group or the benzene ring; R2 was the alkyl and alkoxy of H, C1-C18; the catalyst was mainly the organic tin and n-phthalate. The acid could be a unit acid, a binary acid, a polyacid, a mixed acid or a mixture of acid and alcohol.

When the acid was a unit acid, the unit acid could be stearic acid, oleic acid or the lauric acid. The molar ratio between raw materials was 1:0.5-2, preferably 1:1.05. The reaction temperature should be 160-200 degrees.

When the acid was binary acid or anhydride, the adipic acid, phthalic anhydride and maleic anhydride were preferred. The molar ratio of raw materials was 1:0.2-2, preferably 1:0.8. The reaction temperature should be 160-180 degrees.

When the acid was a polyacid, the polyacid could be phosphoric acid, orthosilicic acid, periodic acid, trimellitic anhydride and so on, preferably trimellitic anhydride. The molar ratio of the raw material was 1:0.1-1.2, preferably 1:0.5. The reaction temperature should be 160-180 degrees. The process of the above reaction was to add raw materials and the catalyst into the reactor in proportion, raised the temperature of the reactor to 140-160 degrees, gradually increased the reaction temperature according to the water output of the hydroxyl terminated organic silicon oil reaction in Formula 1, and then kept the temperature and conduct the reaction in stages. Specifically, when the water yield was 0.1-0.3 time of the molar amount of hydroxyl terminated organic silicon oil, the reaction temperature was controlled at 158-162 degrees; when the water yield was 0.3-0.5 time of the molar amount of hydroxyl terminated organic silicon oil, the reaction temperature was controlled should be 178-182 degrees; when the water yield was more than 0.5 time of the molar amount of hydroxyl terminated organic silicon oil, the reaction temperature was controlled at 198-200 degrees. If the acid is p-benzene or m-benzene low active opaque binary acid, when the water yield was more than 0.5 time of the molar amount of hydroxyl terminated organic silicon oil, the reaction temperature was controlled at 218-222 degrees.

When the acid was a mixed acid, the mixed acid mainly consisted two acids, which could be the mixture of unit acid and binary acid, the mixture of unit acid and polyacid, and the mixture of polyacid and binary acid. The ratio of mixed acid was 2:8-8:2, preferably 4:6-6:4. The reaction temperature was 140-200 degrees. When the isophthalic acid or the terephthalic acid was involved in the reaction, the experiment followed a step-by-step method because of their low activities. The researcher needed to ensure the complete reaction transparency of benzene or isophthalic acid through adding excessive hydroxyl functional groups. If the hydroxyl functional groups were added at the same time, the product might become opaque or poor permeability due to the insufficient content of hydroxyl functional groups at the later stage of the reaction.

This study also included another method of preparing the polyester modified organic silicon levelling agent. Under the premise of excessive acid, $\text{HO}[(\text{R}_1)_2\text{SiO}]_n\text{R}_2$ reacted with acid to generate $\text{HOOC}[(\text{R}_1)_2\text{SiO}]_n\text{R}_2$ and alcohol, and further reacted to generate polyester modified organic silicon levelling agent.

The alcohol was a common binary alcohol or polyhydric alcohol in this field; the acid could be an organic acid or an inorganic acid commonly used in the field. The molar ratio of $\text{HO}[(\text{R}_1)_2\text{SiO}]_n\text{R}_2$, alcohol and acid was 1:1-2.0:1-2.0, in which the reaction temperature with acid was 140-180 degrees for 2-3 hours; after adding the alcohol, the reaction temperature was 160-200 degrees for 2-3 hours. Then the polyester modified silicone levelling agent was obtained.

In the above reaction, acid and alcohol could react to form carboxyl prepolymer first, and then the prepolymer reacted with hydroxyl terminated organic silicon oil to obtain linear polyester organic silicon oil.

The reaction process was as follows. The acid and alcohol reacted first to form polyester prepolymer, and then polyester prepolymer reacted with it to form the polyester modified organic silicon levelling agent.

The molar ratio of $\text{HO}[(\text{R}_1)_2\text{SiO}]_n\text{R}_2$, acid and alcohol was 1:1-2.0:1-2.0, in which the reaction temperature of acid and alcohol was 140-200 degrees for 3-4 hours. After cooling, $\text{HO}[(\text{R}_1)_2\text{SiO}]_n\text{R}_2$ was added the reaction temperature raised to 140-180 degree for 2-3 hours; then the polyester modified organic silicon levelling agent was obtained.

The above technical scheme including alcohol and acid could achieve the same effect when the acid reacted with the organic silicon oil or the alcohol first.

2.3 Specific Experiments

This part further describes the experiment. It should be noted that under the premise of no conflicts, each example and each technical feature described below can be arbitrarily combined to form a new example. The raw materials in the examples can be obtained through the market.

The example 1 used monoacid.

According to the molar ratio of 1:1.2, 90g $\text{Si}(\text{CH}_3)_3\text{-OH}$ and 240g lauric acid were weighed respectively and added to the reactor. Then the temperature was raised to 200 degrees; materials were stirred and reacted for 3 hours. The next step was reduced pressure distillation at the vacuum degree of 0.09MPa to remove low-boiling-point substances. At last, 274.6g polyester modified organic silicon levelling agent 1 was obtained. The yield coefficient was 88%. The agent was called as poly 1 for short.

The example 2 used binary acid.

According to the molar ratio of 1:0.8, 276g $\text{Si}(\text{CH}_3\text{O})_3\text{-OH}$, 236.8g phthalic anhydride and 0.25g n-butyl phthalate as the catalyst were weighed respectively and added to the reactor. Then the temperature was raised to 180 degrees; materials were stirred and reacted for 3 hours. The next step was reduced pressure distillation at the vacuum degree of 0.09MPa to remove low-boiling-point substances. At last, 391g polyester modified organic silicon levelling agent 2 was obtained. The yield coefficient was 79%. The agent was called as poly 2.

The example 3 used polybasic acid.

According to the molar ratio of 1:0.3, 321g $\text{Si}(\text{C}_7\text{H}_8)_3\text{-OH}$, 57.6g trimellitic anhydride and 0.30g organic tin as the catalyst were respectively weighed. The process of the reaction was to add raw materials and the catalyst into the reactor and raise the temperature slowly. Then the researcher weighed and took the product water of the water separator according to the different activity of carboxyl groups. When the water yield was about 5.4g, the reaction temperature was controlled at 143 degrees; when the water yield was about 10.8g, the reaction temperature was controlled at 157 degrees; when the water yield was about 14.4g, the reaction temperature was controlled at 180 degrees, and then kept for 2 hours. The next step was reduced pressure distillation at the vacuum degree of 0.09MPa to remove low-boiling-point substances. At last, 328g polyester modified organic silicon levelling agent 3 was obtained. The yield coefficient was 91%. The agent was called as poly 3.

The example 4 used mixed acid.

The mixed acid was composed of lauric acid and trimellitic anhydride; the researcher weighed 40g and 38.4g respectively according to the molar ratio of 1:1. Then 321g $\text{Si}(\text{C}_7\text{H}_8)_3\text{-OH}$ (the molar ratio with the mixed acid was 1:0.4) was added to the reactor. The mass of butyl phthalate catalyst is 0.1% of the $\text{Si}(\text{C}_7\text{H}_8)_3\text{-OH}$, namely 0.321g. The reaction temperature was 150 degrees. Materials were stirred and reacted for 3 hours. The next step was reduced pressure distillation at the vacuum degree of 0.09MPa to remove low-boiling-point substances. At last, 305.2g polyester modified organic silicon levelling agent 4 was obtained. The yield coefficient was 80%. The agent was called as poly 4.

The example 5 used acid and alcohol.

According to the molar ratio of 1:1, 104g of neopentyl glycol and 148g of phthalic anhydride were weighed respectively and added to the reactor. Then the temperature raised to 180 degrees; materials reacted for 2 hours. Then the materials were cooled to 100 degrees; 276g $\text{Si}(\text{CH}_3\text{O})_3\text{-OH}$ was added. Then the materials were slowly heated to 160 degrees for 3 hours. Finally, 340g polyester modified organic silicon levelling agent 5 was obtained with the yield of 69%. It was called as poly 5.

The contrast example 1 is the Songyuan BYK310 polyester modified organic silicon levelling agent produced by BYK Chemie, which was called as contrast 1 for short.

The contrast example 2 is the Dowcorning DC57 organic silicon levelling agent purchased, which was called as contrast 2.

The contrast example 3 is the ShinEtsu X-22-176F organic silicon levelling agent made in Japan, which is called as contrast 3.

The example 6 is the performance evaluation.

The composition of the baking paint in this experiment was determined with reference to the test formula of the paint system. In this experiment, the ratio of polyester resin: titanium dioxide: ethylene glycol ether acetate was 60:20:20; the materials were grinded and dispersed.

According to 0.2 parts of the baking paint, polyester modified organic silicon levelling agents in examples 1-5 and contrast examples 1-3 were added respectively. The agents were stirred evenly, and applied on the aluminium plate with the size of 11cm * 7cm * 0.2cm. The paints were dried at 150 degrees for 5 minutes, and baked at 280 degrees for 10 minutes. Then the materials were solidified into films; the 23µm thick films were obtained.

First is the levelling property evaluation. The 20° glossiness of the coating film was measured by the fog shadow gloss meter. The higher the glossiness value is, the higher the glossiness of the coating film will be. The wave scan-dual was used to measure the distinctness of image. The higher the DOI value is, the smoother the surface of the coating film will be.

Second is the heat resistance evaluation. Colour changes on the coating surface were visually identified, with 1-5 indicating the degree of yellowing. 1 indicates no yellowing; 5 indicates severe yellowing.

Third is the friction evaluation. Levelling agents were scraped on the glass plate, dried at room temperature and then dried at 125 degrees for 40 minutes. Before measurement, the coating was kept at room temperature for 24 hours. The Ray Ran microprocessor system was used in the test. The machine carried a weight of 200g through the coating and measured the friction coefficient N.

The performances of levelling agents in examples 1-5 and contrast example 1-3 were compared; the results were shown in the following table.

Table 1 Performances of Levelling Agents in Examples 1-5 and Contrast Examples 1-3

group	Poly 1	Poly 2	Poly 3	Poly 4	Poly 5	Contrast 1	Contrast 2	Contrast 3
DOI	98	98	97	96	97	83	85	87
heat resistance	1	1	1	1	1	3	4	2
friction coefficient N	0.18	0.17	0.16	0.17	0.16	0.38	0.42	0.30

From the above table it can be seen, comparing with the contrast groups, after using the polyester modified organic silicon levelling agents prepared in this study, the coating film has better performances in the gloss value and DOI value, indicating that these agents have better glossiness and distinctness of image, and further indicating that the levelling property is better. The tested coating needs to be baked and solidified at 280 degrees; the coating films added with contrast agents went yellow seriously, while the coating film added with polyester modified organic silicon levelling agents prepared in this paper did not go yellow. It shows that these polyester modified organic silicon levelling agents have excellent heat resistance and can resist the temperature of 280 degrees. In addition, the friction coefficient of paint containing levelling agents prepared in this paper was significantly lower than that of paint containing contrasting agents. In general, the performances of the polymer organic silicon levelling agents prepared in this experiment are superior to those of the conventional levelling agents.

3. Conclusion

In the synthesis of polyester modified organic silicon levelling agents, it is found that the yield of the product was high and the process was well controlled. Meanwhile, the prepared polyester modified organic silicon levelling agents used in the paint system have better glossiness, DOI and heat resistance than conventional levelling agents. The product has outstanding performance and good market prospects. At the same time, the levelling agent in this study has low cost; the raw materials are easy to obtain. It has extensive commercial prospects.

With the continuous development of the chemical industry, the application field and scope of coatings are expanding; various innovative materials and additives emerge in endlessly. The development of organic silicon coating additives has made great contributions to the whole coating industry. However, with the continuous improvement of people's aesthetics and a part of harsh

using environment, especially in the context of national advocacy of industrial upgrading and ecological environmental protection, the industry puts forward higher requirements on the performance of products. As a finishing point in the chemical industry, auxiliaries will play a greater role. They can provide more excellent solutions for the construction, engineering machinery, printing and other related industries, make the society develop towards a greener, energy-saving, environmental protection and sustainable direction, and finally make our planet a better home.

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