Preparation of Hydrated Calcium Silicate High Filler Ink and Study on Printing Suitability

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Abstract

In the process of extracting alumina from high-alumina fly ash of power plant, the amorphous silica in fly ash is extracted by alkali solution and precipitated with lime milk to synthesis hydrated calcium silicate powder, which has the characteristics of high oil absorption, high value, low abrasion value, large specific surface area and low bulk density, show that the addition of hydrated calcium silicate filler to the printing ink helps to improve the viscosity, fineness, color density, color and other indicators. The filler filling ratio is higher than traditional ink fillers such as calcium carbonate. It is expected that the hydrated calcium silicate filler has wide potential application value in ink reduction, VOCs control and functionality.

Keywords: High-alumina fly ash; hydrated calcium silicate; filler; ink; printing suitability

Introduction

In printing production, the addition of fillers can act as a substitute for the pigment portion, reduce the cost of the pigment, and it also can adjust the properties of the ink, such as thick, fluid, etc., and improve the flexibility of the formulation design. Conventional ink fillers generally use calcium carbonate powder. The ink formulated with calcium carbonate has good printing performance, fast drying, no side effects, and exhibits excellent dispersibility and transparency in ink products due to its small particle characteristics. As well as excellent ink absorption and dryness, so the printed products are fine, and the dots are complete, but the ultra-fine calcium carbonate used for the ink must be activated. At present, the domestic high-grade ink fillers mostly use ultra-fine calcium carbonate, and the synthesis process is complicated. The cost is high. In order to find a cheap new material that can replace calcium carbonate and reduce the cost of ink, the calcium silicate material used in this experiment has lower synthesis cost, simple process, and siloxy and silanol functional groups on the surface of the material. It has strong reinforcing properties and chemical bonding properties and has strong chemical adsorption properties. The Si-OH contained therein can be Si-OH coupled with the binder and some organic pigments in the ink to achieve silane coupling, thereby achieving a close combination of the calcium silicate filler and the ink connecting material, thereby improving the bonding. The integrity of the ink after filling, and the chemical combination of calcium silicate and volatile organic compounds in the ink, reduce the amount of volatilization into the atmosphere, achieve the effect of controlling the reduction of ink VOC, and achieve the theme of green printing.

2. Experimental

Materials

The preparation methods of calcium silicate fillers are various, and the materials obtained by different preparation methods are also diverse. In this experiment, calcium silicate hydrate was hydrothermal synthesis by disilicate solution mixed with effective calcium solution of lime milk, Reaction conditions was normal temperature and pressure. In the process, sodium tripolyphosphate solution with 1% concentration and 2% addition was added to modify the silicate synthesized after the experiment. Calcium filler, which is characterized by smaller particle size measured by laser particle size analyzer than that obtained by unmodified experiments, is a porous and highly adsorptive inorganic functional material with high whiteness and purity.
It can be seen from the figure 1 and figure 2 that the modified calcium silicate filler has the same crystal structure as the ordinary calcium silicate filler, which belongs to honeycomb flake. However, after modification, the crystal structure is clearer and the whole structure distribution can be clearly seen. The ordinary calcium silicate in Fig. 1 can only be a cloud-like material, while the modified calcium silicate filler in Fig. 2 (mag: 30000) can be clearly seen. Honeycomb flakes were seen, and the surface of the crystal was porous and the structure between layers was clear. This shows that the modified calcium silicate material has better adsorption characteristics than ordinary calcium silicate material, its water content is more than ordinary calcium silicate material, and its binding ability with hydrogen bond and ink filler is greater. Therefore, the performance of ink prepared with modified calcium silicate filler is better than that prepared with ordinary calcium silicate filler.

In the experiment, an ink formula with modified calcium silicate instead of calcium carbonate as filler was used. The replacement rate was 0%, 20%, 40%, 60%, 80%, 100%. The experimental scheme was as follows:

| Table 1 Proportion of Modified Calcium Silicate Filler Ink |
|:---------------------------------------------------------|
| **Ink Proportion** | **Organic Pigment [g]** | **Phenolic Resin Oil [g]** | **Calcium Carbonate [g]** | **Calcium Silicate [g]** | **Ink Modifier [g]** | **Desiccant [g]** | **Antioxidant [g]** |
| A* | 5 | 30 | 10 | 0 | 5 | 4 | 1 |
| B* | 5 | 30 | 8 | 2 | 5 | 4 | 1 |
| C* | 5 | 30 | 6 | 4 | 5 | 4 | 1 |
| D* | 5 | 30 | 4 | 6 | 5 | 4 | 1 |
| E* | 5 | 30 | 2 | 8 | 5 | 4 | 1 |
| F* | 5 | 30 | 0 | 10 | 5 | 4 | 1 |

**Experimental method**

a. The tray balance is used to weigh a certain gram of ink ingredients proportionally. The ink ingredients are added to the beaker according to the weighted proportion. First, liquid substances are added to the beaker, then powder substances are added. Then, the mixture is stirred evenly with glass rods. Then, the mixture is further crushed and stirred in a three-roll grinder. Finally, the crushed ink is put into the beaker for reserve.

b. Adjust the level of NDJ-8S digital viscometer, make the bubble in the instrument in the middle position, ensure that the instrument in the horizontal state, select the appropriate speed and rotor. The suitable drill is screwed
into the drill connector, the ink is placed in the measuring cylinder, and the lifting knob is adjusted to make the ink liquid height equal to the liquid mark on the rotor (the middle of the groove). Click on the measurement to get the viscosity data, move the position, and measure the viscosity data again.

c. Take out a few drops of the ink with a spoon and drop it into the deepest part of the groove, i.e. the maximum part of the scale value. Hold the scraper with both hands, make the scraper contact with the scraper surface at an angle of 45 degrees, and scrape the scraper from the largest scale to the smallest scale. Subsequently, the uniform exposure of particles in the groove was observed by light, and the corresponding calibration values were recorded.

d. The paper strip is pasted on the rectangular strip on the printability tester, placed in the suitable position of the printability tester, the ink is put on the printing drum, the ink rollers rotate and contact each other, when the ink is evenly distributed on each drum, both hands press the buttons on both sides of the machine at the same time, and the printing drum is pressed on the printing wheel to complete printing.

e. The printed pattern is taken off and dried, and the mask layer is completely dried. The data of chroma and color density are measured with a densitometer. Each group of data is measured three times and its average value is measured.

Before checking the ink viscosity, fineness and other indicators, it is necessary to observe with the naked eye whether the fluidity of the ink is good, and whether the fillers added in it can be evenly dispersed in the ink system. If the ink is too viscous, it needs to add proper amount of toner and stir again; if the particle distribution is uneven, it needs to grind again and increase the stirring time.

3. Results and discussion

Measurement and Analysis of Ink Printing Fitness

The color density, chromaticity, tone error and gray data of the modified calcium silicate ink are shown in the following table:

| Ink Proportion Scheme | Color density | Chrominance | Tonal error [%] | Grayscale [%] |
|-----------------------|---------------|-------------|-----------------|---------------|
| A*                    | 1.22          | 98.19       | 20.33           | 24.00         |
| B*                    | 1.33          | 97.37       | 20.50           | 26.50         |
| C*                    | 1.16          | 98.40       | 21.00           | 25.00         |
| D*                    | 1.10          | 98.17       | 19.50           | 24.00         |
| E*                    | 1.06          | 97.96       | 19.00           | 23.50         |
| F*                    | 1.11          | 97.21       | 19.50           | 26.00         |

Analysis results of ink color density

![Color density map of modified calcium silicate ink](image)

It shows that with the increase of calcium silicate substitution rate, the value of color density first increases, then decreases, and then stays in a stable state. The maximum value of color density is 1.33 under the experimental conditions of group B* and then decreases to a stable state. The minimum value of color density is 1.06 in group E* and the maximum value of reduction is 0.27. The color density value of modified calcium silicate ink is above 1, and with the increase of calcium silicate replacing traditional calcium carbonate, the color density value of ink does not change much. So, when water-borne calcium silicate replacing calcium carbonate as filler, the color density value of ink has little influence, and is in acceptable range, and when replacing 20%, the color density value of printed matter is better than that of crude oil ink.

Analysis of Ink Chrominance Results

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It can be seen from figure 4, the chromaticity value changes around 98 with the increase of the amount of modified calcium silicate replacing calcium carbonate. In C* group, the maximum value is 98.4, which is 1.19 more than the minimum value of F* 97.21. The trough performance of B* group curve may be caused by operation errors, but in general, the six groups of experimental values are in a relatively stable state and meet the ink chromaticity standard, so modified calcium silicate can be used as a substitute for calcium carbonate in the analysis of ink printing chromaticity value.

Fig.4 Chrominance diagram of modified calcium silicate ink

Analysis of Hue Error and Grayness Result

From the analysis of hue error, the maximum value of hue error is 21.00% in C* group and 19.00% in E* group. With the increase of the amount of modified calcium silicate replacing calcium carbonate, the whole curve first increases, then decreases, and then increases. The difference between the maximum value and the minimum value is less than or equal to 2%. The value of tone error in D*, E*, F* group is relatively stable, and the value of tone error in D*, E*, F* group is better than that in crude oil ink printing.

From the grayness value analysis, the whole curve first increases, then decreases and then increases. The maximum value of B* is 26.50%, the minimum value of E* is 23.50%, and the difference between the maximum value and the minimum value is 3%. The value is relatively stable. Therefore, the use of modified calcium silicate filler instead of calcium carbonate filler has little effect on the grayness of printing ink and can be used.

Measurement and Analysis of Printing Suitability of Ink

Viscosity and fineness of the modified calcium silicate ink are shown in the following table:
Table 3 Viscosity and Fineness Data Table of Modified Calcium Silicate Ink

| Group | Viscosity |  |  | Average value | Fineness | Average value |
|-------|-----------|---|---|---------------|----------|---------------|
|       | 1         | 2 | 3 |               | 1        | 2             | 3        |
| A*    | 2944.4    | 2988.1 | 3010.1 | 2980.87 | 22 | 20 | 21 | 21.00 |
| B*    | 3119.3    | 3145 | 3210.7 | 3158.33 | 25 | 25 | 25 | 25.00 |
| C*    | 5829.1    | 5821.6 | 5799.5 | 5816.73 | 25 | 23 | 24 | 24.00 |
| D*    | 5424.2    | 5401.1 | 5516.6 | 5447.30 | 22 | 23 | 23 | 22.67 |
| E*    | 5231.2    | 5235.6 | 5343.1 | 5269.97 | 16 | 16 | 17 | 16.33 |
| F*    | 4951.4    | 4921 | 4879.4 | 4917.27 | 13 | 15 | 13 | 13.67 |

Analysis of Viscosity Result

From Figure 6 the whole curve first rose steadily to B* group, then rose rapidly to the highest value of C* group 5816.73 mPa•s, then decreased steadily and slowly to 4917.27 mPa•s, the value of viscosity decreases continuously after the substitution rate is 60%, and abnormal changes have taken place, and its value is more stable and has little change. It can be seen from the figure that the modified calcium silicate filler has a great influence on the ink viscosity, but it can be solved by adding a small number of additives. With the increase of the modified calcium silicate filler, the ink viscosity performance gradually decreases.

Fineness result analysis

Analysis of figure 7 shows that the value of the whole curve first increases to group B* and then slowly decreases. Under the condition of E* experiment, the data obtained sharply decreases to 16.33μm, and when the replacement rate of modified calcium silicate is 100% (F*), the minimum fineness is 13.67μm, which is much smaller than the fineness data obtained under the condition of 0% substitution rate. The change of fineness value should increase gradually, and then reach the maximum value at a point of substitution rate between values of B*C* group, and then decrease gradually. But there may also be manual or systematic errors.
Discussion

From the viscosity data, with the increase of replacement rate of modified calcium silicate filler, the viscosity value is always higher than that of crude oil ink, and the value of C* group decreases steadily, which belongs to the normal ink viscosity range. From the fineness numerical analysis, the experimental data of B* group decreases successively, and the minimum value is much lower than that of crude oil ink, which conforms to the normal ink viscosity range. The numerical values of color density and chroma of ink printed matter show that the values of C* to F* groups decrease in turn, but the reduction values are small, within acceptable range, and all the values meet the printing standards of ink. From the analysis of hue error and gray value, the values of D* group and E* group are relatively small, so the comparison of the above data shows that the replacement rate of calcium carbonate filler by calcium silicate filler is 20%. Under the condition of B* group experiment, the comprehensive effect of the ink is the best. The gradient chosen in this experiment is too large. In 20-40%, there should be a value of substitution rate. The printing performance of the ink is better than that of calcium silicate ink when it is 20%. However, using modified calcium silicate filler instead of calcium orthosilicate filler, the printing adaptability of ink is better than that of crude oil ink, so this calcium silicate filler can be used to replace calcium carbonate filler in crude oil ink.

4. Conclusion

Experiments show that the use of modified hydrated calcium silicate instead of part of the original calcium carbonate as filler is more suitable for ink filling, can improve the filling ratio and reduce printing costs, and can achieve the role of environmental protection and green printing beautification environment. The experimental results show that the performance of the modified calcium silicate ink filler is better than that of the common ink filler.

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