Progress in Organic Coatings 87 (2015) 189–196

Contents lists available at ScienceDirect

Progress in Organic Coatings

journal homepage: www.elsevier.com/locate/porgcoat

Effects of formulation on set-to-touch time of waterborne alkyd resin by uniform design

Quehong Huang[a], Chao Liu[a], Shujun Chen[a], Genghua Bai[a], Qi An[a], Jun Cao[a], Sisi Zheng[a], Yuanpeng Liang[b], Bin Xiang[a,*]

[a] School of Chemistry and Chemical Engineering, Chongqing University, Chongqing 400044, China
[b] Liangjiang Medicine Co., Ltd., Chongqing 401331, China

ARTICLE INFO

Article history:
Received 6 December 2014
Received in revised form 21 April 2015
Accepted 1 June 2015

Keywords:
Alkyd resin
Waterborne
Uniform design
Formulation calculation
SPSS
Optimization

ABSTRACT

In order to optimize the formulation of waterborne alkyd resin preparation, a 9-level-3-factor uniform design and regression analysis were firstly employed to evaluate the effects of the selected variables including fatty acid content (L), hydroxyl/carboxyl molar ratio (r) and molar ratio of polyatomic acids (f) on set-to-touch time of film. The results indicate that the data can be adequately fitted with a first-order polynomial model, and the main factors successively affecting set-to-touch time are fatty acid content (L) and molar ratio of polyatomic acid (f). The above model is proved valid within the designed scopes of the investigated formulation parameters by validation experiments. The optimized formulation parameters for waterborne alkyd resin synthesis is predicated as follows according to the model, i.e. L is 30%, r is 1.2, f is 2.2, the result set-to-touch time is 43 min, which significantly shorten the drying time.

1. Introduction

Since it was synthesized by Kienle in the 1950s [1], alkyd resins have been widely used as binders in paints [2]. Alkyd resins have been used to produce a broad range of coating materials for different uses, such as varnishes, acid curing coatings, anticorrosive coatings, etc. After years of deeply research, the process skills of alkyd resins are sufficiently matured, and the effects of oil and drier on the resin properties have been described by many studies to optimize the paint formulation and improve the film properties [2–6]. So far, several approaches such as combining alkyd with other binders have been reported to achieve greater properties, the most attractive technology was acrylic–alkyd hybrid systems [7–11]. More recently, attention has been focused on developing alkyd-based systems with low or zero volatile organic compounds (VOCs), such as alkyd emulsions and high solid alkyds for environmentally-friendly coatings [2,12–15]. The literatures of alkyd paints about the development of formula design are insufficient to the industrial applications. So, it is necessary to further enrich the research on the formula design.

Calculating techniques for alkyd resin formulating have been developed over the past few decades [16]. There were many attempts to calculate the ratios of functional groups and the extent of reaction that can be reached without gelation, but none was fully successful. The problem is complex. In addition to the difference of the reactivity of the hydroxyl groups, particular emphasis is placed on the extent of formation of cyclic compounds by intramolecular esterification reactions [17]. Till now, several methods have been used to obtain the alkyd formulations [18–21], and K alkyd constant system was quite commonly used. However, the influences of formulation parameters on the coating characteristics and properties have generally been studied by means of empirical approaches or classical one-factor-at-a-time.

Due to water as the dispersion medium with high latent vaporization heat, waterborne alkyd resins generally have much longer drying/curing time than traditional solvent-borne ones, particularly at ambient temperature. We cannot measure any other film properties if the resin film cannot be cured even after a long time drying/curing. So drying time is one of the most prime and important properties to improve for waterborne alkyd resin coating. Moreover, it is very difficult to obtain waterborne alkyd resin both with good water solubility and short drying time although there have been some attempts [9,22,23]. Therefore further studies on the quantitative relationship among set-to-touch time and the formulation parameters need to be carried out to improve drying properties and water solubility simultaneously.

Uniform design is a new method of experimental technique established together by Fang et al. [24]. It has been gradually extended in China, particularly in science researches, military

* Corresponding author. Tel.: +86 023 65102531.
E-mail address: xiangbin@cqu.edu.cn (B. Xiang).

http://dx.doi.org/10.1016/j.porgcoat.2015.06.001
0300-9440/

sciences, and of course, chemistry and chemical engineering. Uniform design allows the amount of levels as many as possible for each investigated factor, moreover, the number of the experimental trials is equal to the maximum number of the levels of the investigated parameters [25,26]. In general, uniform design is preferred since it reduces the number of experiments significantly to evaluate multiple parameters and their interactions. Therefore, it is less laborious and time-consuming to optimize a process than other approaches.

In this paper, uniform design as well as regression analysis was used to study the influence of formulation parameters (fatty acid content (L), hydroxyl/carboxyl molar ratio (r) and molar ratio of polyatomic acids (f)) on the film set-to-touch time of waterborne alkyd resin.

2. Experimental

2.1. Materials

Soybean fatty acid (SFA), trimethylol-propane (TMP), phthalic anhydride (PA), trimellitic anhydride (TMA), and water-based drier were kindly provided by Chongqing Sanxia Paints Co., Ltd. (Chongqing, China). Ethylene glycol butyl ether (EGBE) (AR), triethylamine (TEA) (AR) and xylene (AR) were purchased from Chengdu Kelong Chemical Reagent Company (Chengdu, China). All the materials mentioned above were used as received without further purification.

2.2. Synthesis of waterborne alkyd resin

Waterborne alkyd resin was synthesized with SFA, PA, TMP and TMA through fatty acid method. The reaction was carried out in a 500 mL four-neck round bottom flask equipped with a mechanical agitator, contact thermometer, nitrogen gas bubbler and Dean-Stark piece. Xylene as the azeotropic solvent was added to the mixture of SFA, PA and TMP, and then the reaction mixture was heated to 100–120 °C. Subsequently, the reaction was heated with stirring to 180 °C for 1 h, 190 °C for 1 h. Then the temperature was raised to 200–210 °C at constant rate of 1 °C/min and kept at 200–210 °C. The reactions were followed with acid value test. The acid value was determined by titration of sample dissolved in ethanol–toluene with 0.1 mol/L KOH solution. The polymerization reaction was continued until the acid value came to 13–17 mg KOH/g. After the reaction, TMA was introduced until the temperature decreased to 150 °C. Then the reaction was stirred at 175–180 °C until an appropriate acid value obtained. After that, the crude alkyd was dissolved in EGBE at 120 °C to form 85% (wt.) solution, and neutralized with TEA at 80 °C, diluted with deionized water to 50% (wt.) and adjust pH to 7.5–8.5 with TEA at last.

2.3. Characterizations

2.3.1. FTIR spectroscopy

The FTIR spectrum was recorded on Nicolet MagnaIR550II spectrometer on KBr disks using thin film.

2.3.2. ^1H NMR spectroscopy

^1H NMR spectra was recorded in D_2O at 400 MHz using Agilent 400MR DD2 NMR spectrometer.

2.3.3. Properties of waterborne alkyd resin 50% (wt.)

Water solubility was tested by diluting the resin with deionized water. 5 g sample in a conical flask was gradually diluted with 25 °C deionized water by shaking until small insoluble matter formed. Then the volume of added water was recorded.

Transmittance of alkyd resin dispersion was performed after five times dilution with deionized water by T60 UV–vis spectrophotometer (from PG Instruments Ltd., Beijing, China) at 480 nm with deionized water as the reference sample.

The storage stability of prepared waterborne alkyd resin was evaluated visually by keeping the samples in glass vials for 6 months.

Dispersion stability of samples were conducted by centrifuging in a centrifuge for 15 min at a speed of 3000 r/min.

2.3.4. Physical properties of waterborne alkyd resin film

To evaluate the film properties, waterborne alkyd resin 50% (wt.) and 6% (wt.) drier were used to prepare film. The solutions were casted on different substrate by 60 μm applicators to form the films and dried at room temperature.

Drying time was determined according to ASTM D1640-03 (2009). Scratch hardness was measured with a pencil hardness-testing device according to ASTM D 3363(2011)$^{\varepsilon 2}$. Gloss test was performed by WGG-60 portable specular gloss meter (Toongfuh Guangahou Co., Ltd., Guangzhou, China). The cross-hatch adhesion test was carried out on coated steel plates after 1 week of application according to ASTM D 3359-09$^{\varepsilon 2}$.

2.3.5. Chemical properties of waterborne alkyd resin film

The cured film of alkyd resin prepared on glass substrate was sealed the edges with wax and immersed into acid solutions (0.1 mol/L H_2SO_4), alkaline solutions (0.1 mol/L NaOH), and salt solutions (3 wt.% NaCl) respectively to test the acid, alkaline and salt solution resistance. Then, the appearance of film was observed after immersion for 1, 2, 3, 4, 5, 6, and 24 h.

All tests were repeated three times to confirm the repeatability of the tests.

3. Uniform experimental design

3.1. Fundamentals of formulation calculation

It would really be necessary to calculate formulation for waterborne alkyd resin synthesis because the calculation technique provides an explicit connection between the ingredients and the relevant parameters of alkyd resin such as number-average molecular weight, fatty acid content (oil length), acid number, K constant, hydroxyl/carboxyl molar ratio and hydroxyl number [16]. Nowadays, oil length, hydroxyl/carboxyl molar ratio and K constant are regarded as the key parameters in the formulation design of waterborne alkyd resin [19–21].

(1) Fatty acid content (L): the weight percentage of unsaturated fatty acid vs the theoretical resin production, which is related to the so-called oil length can be expressed by Eq. (3.1)

$$L \times 96\% = \frac{m}{w} \times 100\% \tag{3.1}$$

where m is the weight of the unsaturated fatty acid, w is the theoretical resin production.

(2) Hydroxyl/carboxyl molar ratio (r): the molar ratio of hydroxyl groups with carboxyl groups, as follows.

$$r = \frac{n_{OH}}{n_{COOH}} \tag{3.2}$$

where n_{OH} and n_{COOH} are the total molar of hydroxyl groups and carboxyl groups of all the starting materials, respectively.

(3) K constant [27]: the esterification degree when the resin begins gel, as follows.

$$K = \frac{n_0}{n_{COOH}} \tag{3.3}$$