



Waterborne hybrid alkyd–acrylic dispersion: Optimization of the composition using mixture experimental designs



Mongi Elrebii^a, Amel Kamoun^b, Sami Boufi^{a,*}

^a University of Sfax, Faculty of Science – LMSE, Tunisia

^b Laboratory of Industrial Chemistry, National Engineering School of Sfax, BPW 3038 Sfax, Tunisia

ARTICLE INFO

Article history:

Received 17 March 2015

Received in revised form 4 June 2015

Accepted 5 June 2015

Keywords:

Hybrid resin

Alkyd

Acrylic

Paint

ABSTRACT

VOC-free waterborne hybrid alkyd–acrylic (50/50 wt/wt) dispersions were synthesized by melt condensation reactions between acrylic pre-polymers bearing carboxylic groups and medium-oil alkyd resins, followed by a self-emulsification through the neutralization of the carboxylic groups by an aqueous ammonia solution. A mixture experimental design was used to investigate how formulation components of the hybrid alkyd–acrylic resin affect the properties of the hybrid dispersion in terms of the viscosity of the dispersion, particle size, hydrolytic stability, and coating performance, namely gloss and film hardness. It was found that the content of ionizable monomers is the dominant factor controlling the particle size. This latter was shown to meaningfully affect the gloss of the coating after drying. The viscosity of the dispersion was mainly governed by the content of the soybean oil fatty acid which also controlled the hardness of the coating film after drying. An optimal composition that fits the requirement of paint formulation in terms of particle size, viscosity, hardness, and gloss was defined on the basis of the results of the mixture experimental design.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Over the past two decades, government regulations, environmental consciousness and customer preferences have pushed the coatings industry to reduce and even completely ban VOCs in coatings formulations. Varieties of approaches have been adopted in an effort to lower VOC levels. Among these approaches: alkyd emulsions [1], polyurethane [2] and acrylic dispersions [3] which are the most widely available and popular systems that fulfill the various end-user demands.

Acrylic latex has been used for more than 50 years as a binder for flat coating. However, the addition of a coalescing solvent to temporarily plasticize and aid in the film-formation process is essential. The level of this coalescing solvent might exceed 20% based on the latex dispersion, especially when glossiness is sought [4]. Moreover, given the high molecular weight of the polymer within the latex particles, the viscosity is high and the flow ability is low even in presence of a coalescing agent. This results in a low leveling, poor substrate wetting, low adherence and low film gloss [5]. Besides, the presence of surface active agents, necessary for

the processing of acrylic dispersions, contributed to further impair film properties such as gloss, stain blocking and water resistance [6,7].

The alkyd emulsions provide the advantages of alkyd chemistry such as good flow and leveling, superior substrate wetting properties, good adhesion and good gloss development. In addition, alkyd dispersion undergoes crosslinking through the traditional oxidative mechanism bringing increased hardness over time [8,9]. However, alkyd resins suffer from limited hydrolytic stability, alkali resistance and long drying times.

One approach to alleviate the shortcoming of each component and create a highly performing class of waterborne binders is to combine these two polymers in a hybrid system consisting of a chemical blend of acrylic–alkyd dispersions [10,11]. The chemical hybridization of acrylic and alkyd structures is expected to provide the advantages of acrylic polymers such as hardness, gloss, weatherability and chemical resistance, and also the advantages of alkyds such as good adhesion, high gloss and good penetration. Furthermore, given the low glass transition of the alkyd backbone, there is no need to add the coalescing solvent in order to ensure good film formation [12].

In our previous work, self-emulsifying hybrid acrylic–alkyd waterborne dispersions, exempt of any added solvent or surfactant were synthesized by melt condensation reactions between oil-modified acrylic pre-polymers and medium-oil alkyd resins,

* Corresponding author at: University of Sfax, Faculty of Science, BP 1171-3000 Sfax, Tunisia. Fax: +216 74 274 437.

E-mail address: Sami.Boufi@fss.rnu.tn (S. Boufi).

followed by an emulsification through the neutralization of the carboxylic groups by a base [13]. The effects of the carboxyl content and the anhydride addition on the particle size, the colloidal stability and the viscosity of the dispersions were investigated. It was shown that the carboxylic charge density and the presence of maleic anhydride in the acrylic pre-polymer controlled the long-term stability of the colloidal dispersion. The usefulness of the waterborne hybrid dispersion as a binder to prepare air-drying water dilutable paint without any VOC or coalescent agent was also shown.

To gain further insight on how the chemical composition of the hybrid resin is likely to affect the particle size of the dispersion, its viscosity, the surface property and the long term stability, a specific composition of the hybrid resin is retained as reference and a four-component mixture experimental design has been applied in the surroundings of the retained composition. The properties of paints in terms of gloss, drying time and hardness were also investigated through this approach. The objective is to generate a model that provides an adequate description of the changes in properties of both the dispersion and the resulting coating film to variations of the composition of the hybrid dispersion.

2. Materials and methods

2.1. Materials

Pentaerythritol (Penta, Perstorp, Sweden), phthalic anhydride (IPA, Aldrich, Steinheim, Germany), benzoic acid (BA), soybean oil fatty acid (SFA), di-terbutyl peroxide (Trigonox B, Akzo Nobel) were used directly without further purification. Methyl methacrylate (MMA) (99.5%), ethylhexyl acrylate (EHA) (99.5%), methacrylic acid (MAA) (99.5%), maleic anhydride (MA), cobalt(II) nitrate hexahydrate, zirconium(IV) nitrate and xylene were purchased from Aldrich. All materials were used as received.

2.2. Preparation of the alkyd resin

The alkyd resin, with a low molecular weight and an oil length of 50%, was prepared by polycondensation as follows: the mixture of xylene, soya fatty acid, phthalic anhydride, benzoic acid and pentaerythritol was charged in a glass reactor equipped with a thermometer, mechanical stirrer, Dean-Stark apparatus and nitrogen gas inlet. It was slowly heated up to 230 °C and maintained under azeotropic distillation until a low acid value was reached (about 8 mg KOH/g). The xylene was, then, removed by stripping under low pressure and the resin was cooled. The recipe of the medium alkyd resin and its physical characteristics are shown in Table 1.

Table 1
Recipe and properties of the alkyd resin used for the preparation of the hybrid alkyd–acrylic dispersion.

Composition	Weight (%)
SFA	46
PENTA	23
IPA	22
BA	9
Characteristics	
Oil length	51
Acid number, mg KOH/g	7
Hydroxy number, mg KOH/g	105
Viscosity (25 °C) 100 wt%, mPa s	
M_w	2200

2.3. Preparation of the acrylic–alkyd waterborne dispersion

The preparation of the hybrid dispersion was similar to that reported in our previous work [13]. In brief, fatty-acid modified acrylic copolymers were first prepared by free radical polymerization. The soya fatty acid was first charged into a reactor and heated to 80 °C then the acrylic monomer mixture, initiator, and transfer agent were gradually added during 3 h at a constant feed using a peristaltic pump. Polymerization was carried out at 110 °C until complete conversion of the acrylic monomers to yield a light yellowish and transparent viscous solution.

The acrylic copolymer and the alkyd resin were then charged into a three neck round glass reactor equipped with a mechanical stirrer and heated to 180 °C under reduced pressure (10^4 Pa) until a clear melt with an acid value of 35–45 mg KOH/g was obtained. The mixture was subsequently cooled to 120 °C and emulsified by a phase inversion process. This latter was carried out by progressively adding water containing aqueous ammonia, or another base, in a proportion of 1 mol per equivalent of carboxyl groups. The product was a low viscous, opaque-to-translucent dispersion of the water-reduced acrylic–alkyd resin with a solid content of 40 wt%.

2.4. Characterizations

2.4.1. Viscosity

Viscosity measurements of the dispersions were performed at 25 °C using a Haake DC3 equipment working over the range of shear rates of 0–100 s^{−1}. A ‘cup and bob’ set-up was used for these experiments.

2.4.2. Particle size determination

The particle diameter was measured at 25 °C using a Malvern Nano-Zetasizer ZS Instrument working at a fixed scattering angle of 173°. The dispersion was diluted to about 1 wt% with distilled water before starting the measurements. The cumulate average, obtained from the dynamic light scattering (DLS) correlation curve, was fitted with a single exponential decay to determine the particle size distribution. Each measurement was performed in triplicate and the ensuing values were averaged to obtain the mean particle size.

2.5. Paint preparation

Water-based paints were prepared at a pigment volume concentration (PVC) of 15, using titanium dioxide (rutile) as a pigment. A slurry of pigment was first prepared using a laboratory high-speed disperser in the presence of the polycarboxylic based dispersant (DisperByk from BYK). Then, the waterborne hybrid-dispersion was added to the pigment slurry using the disperser at slow speed, and the final viscosity was adjusted by the addition of the associative thickener Coatex-Br100 from COATEX. A mixture of Co and Zr driers was directly added to the pigment slurry suspension just before the binder (the cobalt concentration was typically 0.05% (w/w) per alkyd) (Table 2).

2.5.1. Film formation studies

Films with wet-film thickness of 100 μm were coated on a glass plate using a cube film applicator. The drying time was measured according to ASTM D5895-03 at 23 °C and 50% humidity using a speed-drying recorder. The surface-dry value is the time taken when the needle started to lift out of the bulk film and skimmed along the surface leaving a faint and irregular trace. At this time, the surface was also finger-touch dry.

Specular gloss was determined at 60° using a two-angle gloss-meter from BYK, according to ISO 2813.

Download English Version:

<https://daneshyari.com/en/article/7106922>

Download Persian Version:

<https://daneshyari.com/article/7106922>

[Daneshyari.com](https://daneshyari.com)