Effect of thermal and redox initiator on emulsion copolymerization of styrene – butyl acrylate and comparison of paint properties

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Emulsion copolymerization of styrene with butylacrylate was carried out by thermal and redox initiator. The effect of initiator on molecular weight of the polymer and performance of surface coatings has been described.

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Introduction
Styrene and acrylic binders are used for manufacturing of exterior textured and smooth paints. The copolymer of styrene with butyl acrylate (BA) is widely used as binder for paint. This paper presents the effect of redox and thermal initiator on preparation of emulsion co-polymer of styrene with BA, and the performance of coatings. Redox initiator, potassium persulfate (PPS), sodium meta bisulfite (SMBS) and thermal initiator, ammonium persulfate (APS) are used in emulsion copolymerization of styrene with BA.

Experimental Procedure
Raw Materials
Styrene and BA were purified by washing with 4% NaOH solution and subsequently washed with distilled water. Then the monomer was dried with molecular sieves and distilled under vacuum. Other raw materials, Neopon ANP – 30 (Dai Ichi Karkaria Ltd, Pune), Lissapol 3070 (ICI Uniqema Ltd), IGSurf 8505 (India Glycols Ltd, Kashipur), Maxemul 6106 (ICI Uniqema Ltd), Noigen, EP 120 (Dai-Ichi Karakaria Chemicals Ltd, Pune), methacrylic acid and butyl cellosolve (SD Fine Chemicals Ltd), and PPS, SMBS and Mergal K 9N (Troy Chemicals, Gmbh) were used as received.

Polymerization
Semi batch emulsion copolymerization of styrene-butyl acrylate was performed in a glass reactor (2 l) equipped with a mechanical stirrer, a nitrogen inlet and a thermometer inlet. Glass reactor was placed in a water bath for controlling temperature of reactor. Water phase was charged to the reactor as per recipe (Table 1) and the temperature of water phase was raised (80-82°C). Sodium bicarbonate solution was added to the reactor followed by catalyst solution and seed quantity of pre-emulsified monomer (30 g) was also added. After 15 min, feeding of remaining pre-emulsified monomer was carried out for 3 ½ h and the temperature was maintained at 80-82°C. Reaction was carried out at 84°C for another 1 h. The reaction mixture was cooled to room temperature and other additives were added. Finally, product was filtered with nylon mesh.

Characterization
Mechanical stability of an emulsion is its resistance to particle agglomerisation by high shear motions. Emulsion polymer was stirred at 10000 rpm for 10 min using a mechanical stirrer. Emulsion film was drawn on a glass plate by variable thickness film applicator to check the film properties and the wet film was dried at 30°C for 24 h.

Physical Parameters
Percent solids or non-volatile content was determined by heating samples (2 g) at 120°C for 1 h and weighing the residue. Particle size was determined using LASER diffraction technique (Master Sizer 2000). Viscosity of emulsion polymers was determined by Brookfield Viscometer (RVT Model) at 30°C. The pH of emulsion polymer was...
determined using pH meter. Minimum Film Forming Temperature (MFFT) of polymer was determined by Digital Sheen Instrument (Model No. MFFT BAR 2000). To measure water resistance, dried film was dipped in distilled water. Whiteness found with time gave ratings for water resistance.

To measure alkali resistance, dried film was dipped into 0.1 N NaOH solution. The amount of polymer lost, calculated after 24 h by weight difference of initial and final weight, gave alkali resistance. For Ca\textsuperscript{2+} stability, 2 ml of 10% CaCl\textsubscript{2} solution was added to 10 ml of emulsion. If no grits were formed, then the emulsion is stable. For alkali stability, 2 ml of 10% ammonia solution was added to 10 ml. The absence of grits ensures alkali stability. Molecular weight of polymers was determined by Gel Permeation Chromatography (Water, USA).

**Preparation of Surface Coatings**

Water based decorative exterior smooth paint (PVC, 43%; non-volatile matter, 57%) was prepared using following ingredients: Indofil-731 (dispersing agent), 1.00; Alphox 200 (wetting agent), 0.50; water, 11.50; diethylene glycol, 1.30; biocide (mergal K9N), 0.15; Natrosol HBR solution (3.5%), 2.00; defoamer (Sapco NDW), 0.20; TiO\textsubscript{2} (Rutile), 20.00; China clay, 4.00; talc, 10.00; mica, 3.00; ammonia (20%), 0.20; and emulsion, 33.00 g. Pigments were dispersed with a High Speed Disperser at 2000 rpm and then emulsion polymer was mixed with pigment slurry.

**Evaluation of Exterior Smooth Paint**

Opacity was studied by evaluating contrast ratio (K/S) value. Paint film was drawn on glass plate (wet film thickness, 150 \( \mu \)) and dried for 24 h. The gloss was measured using a Digital Gloss Meter (Sheen, UK). To check washability of the paint, ASTM method (D-2486) was followed. In this method, paint film was drawn on Leneta Sheet (wet film thickness, 150 \( \mu \)) and dried at room temp. for 7 days. The wet scrub resistance was measured using a Wet Scrub Tester (Sheen, UK). The results are given by number of cycles resisted by the film before the film was washed away. For water resistance, dried paint film on glass plate was dipped into deionized water and checked adhesion failure with glass with time.

**Results and Discussion**

**Physical Properties of Binders**

Polymer prepared by redox initiator is more water sensitive than the polymer made by thermal initiator (Table 2). The weight average molecular weight of polymer made by redox system is higher than that of polymer made by thermal initiator. In polymerization, polymerizable surfactant (Maxemul6106) was used. Viscosity of emulsion polymers (Exp. 2 & 4) made with polymerizable surfactant was found higher than the polymers (Exp. 1 & 3) made without copolymerizable surfactant. With thermal initiator, the rise in viscosity was pronounced. Water resistance property of polymer was better with thermal initiator. Other properties, Ca\textsuperscript{2+} stability, alkali stability and alkali resistance, are similar.

**Performance Comparison of Emulsions Made with Redox and Thermal Initiators in Exterior Smooth Paint**

Emulsion polymers prepared with redox and thermal initiator were used as exterior paint binders. Wet scrub resistance of paint made by...
thermal initiator was less than that of polymer made by redox initiator (Table 3). Opacity and gloss were almost similar in each case. Water resistance of emulsion paint prepared from copolymerizable surfactant was excellent.

Conclusions

Styrene butyl acrylate binder was prepared by thermal as well as redox initiator. The molecular weight of polymer made by redox system was higher than that of polymer made by thermal initiator. Wet scrub resistance of paint made by thermal initiator was less than the paint made by redox system. Polymer made by copolymerizable surfactant gave better properties over the commonly used surfactants. Polymer prepared by redox initiator is more water sensitive than the polymer made by thermal initiator.

References