Effects of freezing and thawing on the microstructure of latex paints

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ABSTRACT

Freeze–thaw (FT) cycles can aggregate particles in aqueous paint suspensions. To understand the mechanism of particle aggregation, cryogenic scanning electron microscopy (cryoSEM) was used to visualize the microstructure after the freezing and thawing steps of the FT cycle. After the freezing step, cryoSEM images show that the microstructure contains ice crystals and particle-rich regions. Adding propylene glycol, a FT stabilizing additive, leads to formation of larger ice crystals. After thawing, the dispersion structure revealed by cryoSEM shows that the particles redisperse only in the paint with the highest amount of propylene glycol. The other paints contain clusters that are different from the particle-rich regions found after the freezing step. Increasing the thawing rate leads to a more dispersed microstructure even in the absence of propylene glycol. Analysis of the cryoSEM results shows that particle aggregation into these clusters occurs during the thawing stage, and slow thawing conditions lead to more aggregation. The cryoSEM results reported here are used to propose a mechanism of aggregation of particles in the paint.

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1. Introduction

Latex paints have complex formulations and must meet multiple performance criteria. The main components in the formulation are polymer latex binder, pigment, typically titanium dioxide particles, and water. When an aqueous latex paint is transported or stored in a cold environment, it may freeze and solidify. On thawing, the paint can become coagulated or gelled, a change that is linked to destabilization of the dispersion during the freeze–thaw (FT) cycle [1]. Preventing freezing is not practical; therefore, formulations must be modified so that the dispersion remains stable during freezing and thawing so that the paint application behavior and properties are not compromised. Traditionally, FT stability is imparted by additives, such as glycols; however, environmental concerns and legislative measures have restricted the amount of volatile organic compounds (VOCs), including glycols, allowed in the paint. VOC content is measured as grams of VOC per volume of solids in the suspension. Typically, the VOC level in latex paint is between 100 and 250 g/l [2]. To design around a lower-VOC requirement (<50 g/l) and achieve FT stability, a better understanding of the mechanism of FT stabilization is needed.

The current state of research in FT stability is based on relatively few empirical studies. The general approach is to freeze the paint in a metallic container in a freezer, thaw it under ambient conditions, and observe the change in the suspension structure by optical microscope [3] or measure its rheological properties [4]. While there is an ASTM standard test for FT stability [4], it is qualitative and does not lend itself to research. Therefore, researchers frequently develop their own procedure, which makes it difficult to compare data in literature and develop a generalized understanding of the phenomenon.

An understanding of microstructural changes during freezing and thawing has implications in other fields as well such as cryopreservation of biological samples and food [5,6], remediation of contaminated land [7], and fabrication of nano- or micro-structured materials [8]. However, FT behavior of paints is unique due to slow freezing and thawing conditions. Blackley [1] and Zhao et al. [9] have reviewed the literature for FT stability of latex suspensions. The factors that affect the FT stability of suspensions range from environmental factors, like freezing and thawing conditions, to constitutional factors, like particle chemistry. Some authors have determined that polymer glass transition temperature does not have any correlation with FT stability [10,11], but these claims have also been contradicted in other work [12]. The surface chemistry and presence of hydrophilic groups on the particle surface have been shown to enhance FT stability [13]. Comparatively, freezing and thawing conditions and level of VOC additives have received little attention. Furthermore, no experimental technique has been used to elucidate microstructural changes in paint that occur *during* the FT processes.

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Cryogenic scanning electron microscopy (cryoSEM) has emerged as a unique method to visualize the evolution of microstructure in aqueous suspensions during a process. For example, it has been used to study various stages of drying in particulate [14,15] and polymer coatings [16], morphology and phase behavior of polymer solutions [17,18], cryopreservation of biological samples [19], and freezing of food products [20,21]. The biggest advantages of cryoSEM are that it immobilizes the particles in the aqueous suspension and enables visualization of the frozen sample under high vacuum conditions in the SEM chamber. Immobilizing the suspension at various times during a process allows observation of a complete time sequence of the process. These advantages make it possible to use cryoSEM to study the FT stability of paint. Recently, Zhao et al. [9] used cryoSEM to show that slow freezing rate, slow thawing rate, low freezing temperature, and long freezing times all contribute FT instability. They characterized the microstructure of the thawed paint at the end of the FT cycle. Their data revealed the general effects of freezing and thawing rates on the microstructure; however, the rates were not quantified and only thawed structures were examined.

From research to-date, destabilization during a freeze–thaw cycle appears to be linked to the segregation of particles and additives as ice crystals form. The resulting "freeze-concentration" of particles forces the particles into close-contact with each other and destabilizes the suspension [9,22]. This process can occur either during one FT cycle or over several cycles. Zhao and coworkers also postulate that during slow thawing, ice at the particle interface melts first. The inter-particle space also contains high concentration of ionic species due to freeze-concentration. This causes electrostatic destabilization of the suspension during thawing. However, no study to-date has conclusively proven whether the destabilization occurs during freezing or thawing and correlated the mechanism of aggregation with microstructural changes that occurred during the entire FT cycle.

In this work, we use cryoSEM to study the effect of freezing rate, thawing rate, and the amount of propylene glycol additive on the microstructure of model paints at two points during the FT cycle. The paint is frozen and thawed in a controlled rate freezer; the microstructure of the paint is characterized at the end of the freezing step and at the end of the thawing step in a FT cycle. The effects of propylene glycol content as well as freezing and thawing rates are explored, and the results are used to propose a mechanism for FT destabilization.

2. Experimental methods and materials

2.1. Paint formulations

Acrylic paint samples were formulated by The Dow Chemical Company. A description of the particles present in the aqueous paints is given in Table 1, and cryoSEM images of the particles are shown in Supplemental information. The acrylic binder accounts for 95% of particles on a number basis. Pigments and other particulate additives account for the remaining 5%. For a systematic study on the effect of VOC additive, three formulations with increasing VOC content were prepared:

1. *NA* – a "no additives" model paint with no FT stabilizing additives.
2. *75 VOC* – the model paint with 75 g/l propylene glycol.
3. *150 VOC* – the model paint with 150 g/l propylene glycol.

The total solids content in all three paint samples was 50% by weight or 38% by volume. In addition to the particles, other additives (<2 wt.%) in the paint were the following: silicone defoamer, sodium hydroxide, Optifilm 400 (plasticizer, Eastman Chemical),

Table 1
Summary of characteristics of particles in the paint dispersions.

Type	Average size (nm)	Shape	Amount in dispersion (wt.%)	Number fraction[a] (%)
Titanium dioxide	360	Non-spherical	22.7	1.9
Acrylic binder	150	Spherical	22.4	94.8
Nephyline syenite	2900	Unknown	1.4	<0.1
Styrene acrylic opaque polymer	380	Spherical hollow	0.9	0.2
Attapulgite clay	300–500	Acicular	0.5	3.1

[a] Estimated using the particle density and average size.

and ACRYSOL™ Rheology Modifier (The Dow Chemical Company). The final VOC contents in the NA, 75 VOC, and 150 VOC paints were 7.2 g/l, 75.2 g/l and 149 g/l, respectively.

2.2. Specimen preparation and cryoSEM imaging

To study the effect of freezing (or thawing) on the microstructure of the paint by cryoSEM, small specimens are required. Two brass freezing hats or planchets (Type A, Ted Pella, Redding, CA) were used to make a cylindrical "mini-can" (diameter = 3 mm and height = 300 μm) to contain the dispersion during freezing and thawing. Before specimen preparation, paints were sonicated and approximately 4 μl of paint was loaded into one of the planchets and the other was placed on top, pushing out excess dispersion and resulting in adherence by capillary forces. Due to its small size, the specimen temperature quickly equilibrates with the surroundings, thus reducing transient temperature effects.

After initial loading, the specimen follows one of three paths, as shown in Fig. 1. To characterize the initial dispersion structure (path A), the specimen is frozen rapidly in a high pressure freezing apparatus (Bal-Tech AG, Balzers, Liechtenstein). Opposing jets of liquid nitrogen freeze the sample at a rate of approximately 10^4 K/s. The high pressure of this process (2100 bar) increases the viscosity of water, which suppresses ice nucleation and growth. This very rapid freezing vitrifies the water and preserves the dispersion structure. To characterize the microstructure that develops during the freezing step (path B), the sample is placed in a controlled rate freezer (Crysalys PTC-9500, Biogenics, Napa, CA) with a temperature control accuracy of 0.1 °C. Specimens were frozen at a rate between 1 °C/min and 9 °C/min to a final temperature of −20 °C. The frozen sample was then removed from the freezer and immediately plunged into liquid nitrogen to ensure that any liquid remaining is frozen rapidly, and all the contents are solidified for cryoSEM observation. This process will be referred to herein as plunge freezing. Lastly, to characterize the structure of the dispersion after thawing (path C), the specimen is frozen in the controlled rate freezer, as described above, and then thawed at a controlled rate in the freezer. Thawing rates for this research were between 1 and 3 °C/min to a final temperature of 20 °C. Specimens were equilibrated at room temperature for a given amount of time ranging from 0 to 24 h and then frozen in the high pressure freezer to preserve the microstructure of the dispersion.

It is important to note that in this study, specimens are relatively thick and so high pressure freezing is the only route to the amorphous solid water, which we will refer to "vitrified ice" or "vitreous ice." Controlled rate or "slow freezing" in Fig. 1 leads to crystalline solid water, which we will refer to as "ice", "ice crystals", or "crystalline ice".

Before imaging in the cryoSEM, several additional steps were needed. First, the frozen samples were pried open under liquid nitrogen. This fracture revealed the internal structure of the frozen