THE INFLUENCE OF COALESCENTS ON FREEZE-THAW STABILITY OF STYRENE-ACRILATE LATEX SYSTEMS

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Abstract: It is well known that the correctselection of raw materials is the key to develop the optimal formulation of paints and coatings with the required properties. This work is especially difficult when creating paint formulations with high freeze-thaw stability. To obtain high-quality coatings on their basis, it is extremely important to choose the optimum coalescent for the given latex system, its quantity and technology of introduction. In present paper, a comparative characteristic of widely used coalescents are given. The cryo-SEM results reported here are used to propose differences of the mechanism of coagulation.

Keywords: Freeze-thaw stability, Coalescents, Latexes,VOC, Cryogenic SEM.

I. INTRODUCTION

One of the significant disadvantages substantially limiting wide application ecologically safe waterborne paints is their low freeze-thaw resistance (F/T). The influence of such a coagulating factor as freezing is closely related to the transport and storage of waterborne paints at low temperatures [1], and since a large part of the Earth has harsh climatic conditions with long winter and negative temperatures (-20 to -60°C), then the problem of increasing the F/T resistance of latex is quite acute.Also the issue of transportation and storage of waterborne paints to the regions of Siberia and the Far North is especially acute.

Aqueous dispersions are thermodynamically unstable systems and are far from always reversibly capable of withstanding freezing. From a technical point of view, it is not necessary to identify the latexes before and after freezing and thawing, but only the preservation of working properties [2].When freezing the aqueous dispersions gradual freezing of water, its exclusion from the dispersing medium, which is equivalent to an increase of the particle concentration, the number of collisions, contact time and, eventually, leads to their "violent" contact and irreversible aggregation of the particles.For common latex binders used in paint industry, the glass temperature is around 15-30 ^{o}C, thus coalescing agents are necessary in these formulation to help the film formation. The low F/T resistance is largely latex systems due to the presence in their structure of coalescing additives [3].

Coalescents are commonly used in formulations of waterborne paints, although their usage will decrease due to the low volatile organic compounds (VOC) requirement.With increasing pressure from regulations to reduce VOC in waterborne paints and the push toward low odor coatings, coalescing aids are being taken out of the formulations. At the same time, all coalescents used in present paper classified as non-VOC according to European classification (1999/13/EC and 2004/42/EC) and are of interest for study [4,5,6].

II. DETAILS EXPERIMENTAL

2.1. Materials and Procedures

In order to optimize the composition of the coalescing systems that provide the required level of film formation and the minimum effect on the F/T resistance of aqueous dispersion, a study was made of the influence of the nature of coalescing additives on the freeze-thaw resistance of styrene-acrylate dispersion Finndisp A-10 (Dow Chemical).

The latex has a pH of 7.5, the glass transition temperature is 24, the mass fraction of non-VOC is 51, dynamic viscosity according to Brookfield is 200-1000 mPa*s, withstands without coagulation a standard F/T resistance test (5 cycles at -40 °C, 6 h).

Accordingtheir practical application beginning from heavier to lighter kind of coalescents, they were divided into three groups – Texanol (from Eastman Chemical Company) and UCAR Filmer iBT (from Dow Chemical), Butyl Cellosolve (BC) (from Dow Chemical) and Isopropyl alcohol (IPS)(from Vitahim), Butyl Diglycol Acetate (BDGA) from BASF and Nexcoat NX-795 (from Perstorp).Data of Physicochemical properties of coalescents are given in**Table 1**.

The nature of coalescents was chosen based on the location of their localization in the latex film-forming system: Texanol and UCAR Filmer iBT - in the hydrophobic core of latex particles; BC,IPS - in the aqueous phase; BDGA and Nexcoat NX-795 - in the hydrophilic shell of latex particles.

The coalescents were introduced into the latex with stirring (n = 1000 rpm) and after exposure for 24 hours theF/Tstability was evaluated.

Brand	Composition	Content of non-VOC, %	Freezing temperature,-°C
UCAR Filmer iBT	2,2,4-trimethyl-1,3-pentanediol monoisobutyrate	98,5	50
Texanol	2,2,4-trimethyl-1,3-pentanediol monoisobutyrate	99	50
BC	Ethylene Glycol Monobutyl Ether	99	77
Isopropanol (IPS)	Isopropyl alcohol	99,7	89,5
NexcoatNX-795	Isomer mixture of 2,2,4-trimethyl-1,3-pentanediol monoisobutyrate	99,1	50
BDGA	2(2-butoxyethoxy)-ethyl acetate	99,9	32

Table 1: Physicochemical properties of coalescents

2.2. Visual Test

The test of aqueous dispersion was filled with a can of 6 cm^3 volumes to half the volume, covered with a lid, placed in a freezer and kept for 6 hours at -5 °C to -40 °C, after which the can with the test sample was removed and left at room temperature for 18 hours.The dispersion was then mixed and applied to a glass plate, evenly distributed with a glass rod (test sample).Similarly, a control sample was prepared from the test material that was not subjected to freezing. The test sample was compared with a control sample under diffuse daylight or artificial daylight.The aqueous dispersion was considered F/T resistance if no lumps appeared in the thin layer of the test material [9].

2.3. Determination of the critical temperature of latex coagulation

The F/T stability of aqueous dispersion was characterized by the critical temperature of coagulation (CTC) - the temperature, after which the process of coagulation began (within 1 h). The presence of coagulum was controlled by the content of the mass fraction of non-VOC in the latex after filtration through a metal filter with a pore diameter of 10 mm.

2.4. CryoSEM observation of aqueous dispersions

Cryogenic scanning electron microscopy (cryo-SEM) technology was applied to understand the F/T process of filled by coalescents aqueous dispersions. In this observationwas used SUPRA 55 VP, Carl Zeiss.A CryoSEM technique coupled with a high-pressure freezing apparatus is applied, which makes it possible to visualize nano-structural changes and to study the effects of the freezing and thawing processes separately. It was found that both the freezing and thawing rates have strong impact on F/T stability of polymer latexes, which does not support conclusions from early work with regard to the effect of the thawing process [7,8].

Further study by cryo-SEM shows results in accordance to SAXS measurements in most cases. The cryo-SEM results of samples chosen near phase boundaries between bilayer (*B*), network (*N*) and lamellar (*L*) phases generally show co-existence of two or three phases. Cryo-SEM images of samples chosen from the two phase (*N* + *L*) region show only lamellar structure, which conflicts the SAXS measurement. This could indicate that one or both technique may contain artifacts during the sample preparation, or the certain structure is beyond the imaging capability of the scanning electron microscope.

III. RESULTS AND DISCUSSION

3.1. Influence of the nature and contentof coalescents on freeze-thaw resistance

One of the factors determining the F/T resistance of latex systems is the composition of the dispersion medium. At this stage, was studied the effect of coalescents - one of the most common components in the waterborne paints.**Fig. 1**characterize the influence of the nature of coalescents (at content of 10% on the mass of latex) on the change of the content of non-VOC in latexes after freezing and thawing.

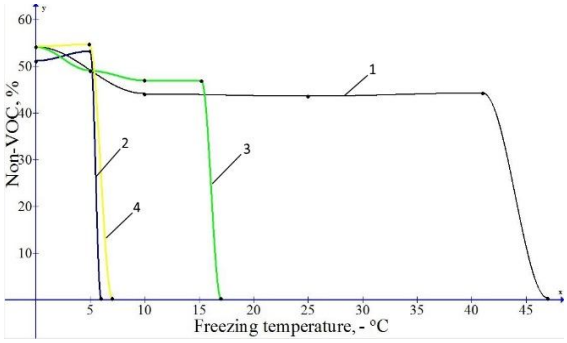

Fig.1a.Dependence of the content non-VOC on the freezing temperature (within 1 h) in the presence of different coalescence: 1 - without coalescence, 2 - Texanol, 3 -BC, 4 – BDGA.

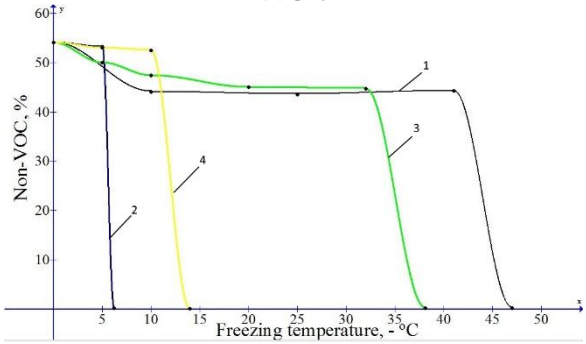

Fig.1b.Dependence of the content non-VOC on the freezing temperature (within 1 h) in the presence of different coalescence: 1 - without coalescence, 2 - UCAR Filmer iBT, 3 - IPS, 4 - Nexcoat NX-795.

Using the obtained data, the critical temperature of latex coagulation (CTC) was determined, the content

of described systemsareshown in the histogram of **Fig. 2.**

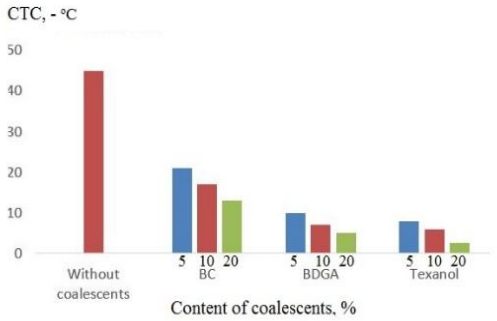

Fig.2. A histogram characterizing the freeze-thaw resistance of aqueous dispersion A-10 in the presence of different coalescents at different contents.

3.2. CryoSEM of aqueous dispersions with coalescents

Specimens were selected to consider the effect in practical application of filled by coalescents aqueous dispersions. It can be seen from **Fig. 3** cryo-SEM images of latex surface BDGA in comparison with IPS coalescent. The first square of cryo-SEM image shows the same imaging like images that was obtained also for other coalescents excluding IPS and Butyl Cellosolve coalescents, but the second image doesn't show any aggregation or/and coagulation.

a) b)

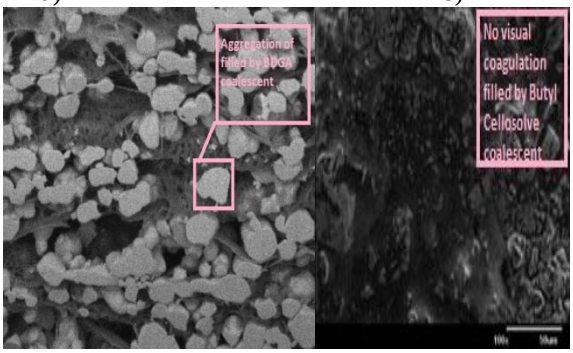

Fig.3.CryoSEM image of the latex surface of BDGA (a) and Butyl Cellosolve (b)

CONCLUSIONS

As can be seen, in the presence of coalescents the F/T resistance of Finndisp A-10 decreases.

1. The degree of reduction in F/T resistance significantly depends on the nature of the coalescents and the location of their localization in the latex system.
2. In the presence of the coalescent, localized in the aqueous phase, isopropyl alcohol, the F/T resistance decreases slightly, and the most significant decrease in F/T resistance is observed for latex containing a coalescent, localized in the nucleus of latex particles - Texanol.
3. Systems containing coalescents localized in the hydrophilic shell of latex particles occupy an intermediate position in F/T resistance.
4. Probably, an acceptable combination of film-forming ability and F/T resistance of latexes can be achieved by using mixtures of coalescents.

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