The Role of Ethylene Glycol and Polyethylene Glycol in the Freeze-Thaw Stability of Synthetic Latex

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Introduction

One of the most important properties of synthetic latex is its freeze-thaw stability, and it is necessary to study this property for industrial application. In the paint industry it is usual to employ the freeze-thaw test in order to determine the stability. Recently Digioia and Nelson[1] have reported freeze-thaw cycles of certain commercial synthetic latices. However, they have not mentioned either the sources or the conditions of the freezing stability. The freeze-thaw test is widely used for the checking of the commerciability of the emulsion, but there is lack of reliable data in quantitative studies concerning it. In the present work the adsorption of ethyleneglycol and of polyethyleneglycol by the emulsion particles of various polyvinyl compounds was studied with reference to the conditions under which freeze stability was attainable.

Experimental

The monomers used are styrene (St.), methylmethacrylate (MMA.), methylacrylate (MA.), vinylacetate (VAc.) and acrylonitrile (AN.). These are purified by vacuum distillation. The polymerization catalyst used is ammonium persulfate, commercial c.p. grade; and the emulsifier mainly employed is sodium-dodecylsulfate, recrystallized twice in ethanol solution. The emulsion polymerization of MMA., MA., VAc. and AN. is carried out at 60°C in still-stand, and that of St. at 80°C in agitation, both for 5 hrs. The concentration of catalyst is 0.1%, and the ratio of monomer to aqueous solution is 0.08.

The freezing process of the emulsion obtained is accomplished by cooling it at -17.5 ± 2.5°C for 24 hrs. If the latex prepared by the addition of glycols is stable enough after its thawing at room temperature, its second freezing is conducted at the same temperature for as many hours, and further its third, if stable, like the second, for 45 hrs. In almost all these cases stability is observed in the second and the third process of the test only when the first process of the test has been satisfactory.

Results and Discussion

1. Preliminary Experiments on the Addition of Ethyleneglycol.—The experiments are shown in Table I. In this table X-marks represent the unstable cases and 0-marks the stable.

TABLE I

EXAMPLES OF THE LATICES OF PVAc. AND PMMA.

Kind of Monomer	Kind (& Amount) of Emulsifier used in Polymerisation	Kind (& Amount) of Stabilizer	Freezing		
			1st.	2nd.	3rd.
VAc.	None	None	x		
"	N. (0.5%)	"	x		
"	A. (")	"	x		
"	K. (1.0%)	"	x		
"	PVA. (0.5%)	"	x	Slightly	
"	None	Ethyleneglycol (5%)	0	x	
"	"	" (10%)	0	0	0
"	N. (0.5%)	" (3%)	0	0	0
MMA.	A. (0.1%)	" (3%)	x		
"	" (0.2%)	" (")	0	0	0
"	" (0.5%)	" (")	0	0	0
"	" (0.5%)	None	x		
"	K. (1.0%)	Ethyleneglycol (10%)	x		

N. Polyethyleneoxide-dodecylether having $\bar{P}=45$
A. Sodium dodecylsulfate
K. Cetyltrimethylammoniumbromide
PVA. Polyvinylalcohol having $\bar{P}=$ca. 1000

1) F.A. Digioia and R.E. Nelson, *Ind. Eng. Chem.*, **45**, 745 (1953).

2. The Minimum Amount of Ethyleneglycol Required for Stabilization.—The freeze-thaw stability can be measured by the determination of the minimum amount of glycol required for the stabilization of the latex. The curves indicating the concentrations of ethyleneglycol versus that of emulsifier are given in Figure 1.

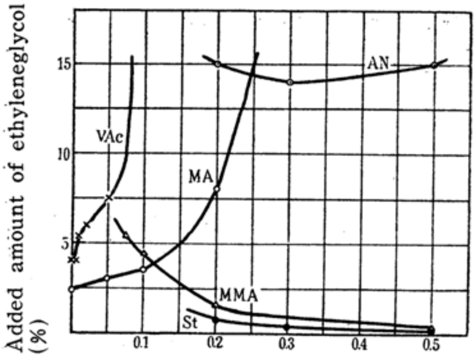

Fig. 1. The minimum amount of glycol required in various types of emulsions polymerized with sodium-dodecylsulfate.

As shown in Fig. 1, these curves are classified into three groups, the first is the case of St. and MMA., the second MA. and VAc., and the third AN. The amount of glycol required decreases in the first groups and increases in the second, and finally is constant in the third, as the concentration of emulsifier increases. In the range of this work, the monomers of the first group are more hydrophobic and those of the second more hydrophilic. An. is most hydrophilic in the monomer state but relatively hydrophobic in the polymer. It may, therefore, be concluded that the facility of stabilization attained by the addition of glycol increases as the hydrophobic property of the monomers or the polymers increases.

From Figure 2 it will be noticed that the amount of glycol required for stabilization is small in the case of using relatively high molecular weight compds, such as polyethyleneglycol as emulsifiers. As shown in the comparison of Fig. 1 and Fig. 2, the freeze-thaw stability is attained more easily in the nonionic than in the anionic detergents. Also in Fig. 2 the order of hydrophobic nature, (St.>MA.>VAc.) is shown as parallel to the order of properties for stabilization.

In all the five monomers the latices obtained with cetyltrimethylammoniumbromide (concentration range 0.7–2.0%) could not be stabilized by the addition of ethyleneglycol (to 20%).

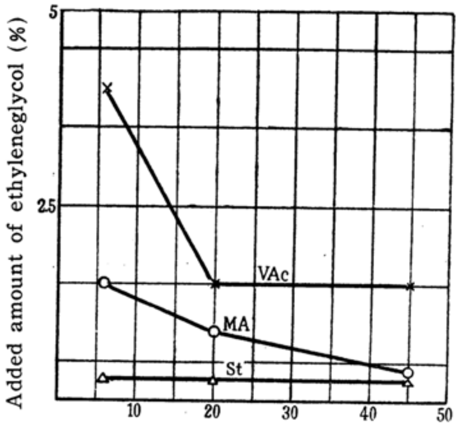

Fig. 2. The minimum amount of glycol required in three types of emulsions polymerized with polyethyleneoxidedodecylether having various degrees of polymerization.

3. The Properties of Stabilized Latices for Freeze-thaw A) Depression of the Freezing Point of Latices.—The value of the freezing point of emulsion must be equal to that of its aqueous solution because the size of its molecules is much larger than of those of the dispersing medium. The depression measurement indicates therefore the decrease of the concentration of glycol in the aqueous solution. Table II represents the comparison of the value of freezing point depression in the aqueous solution of ethyleneglycol and that in the stabilized latices.

TABLE II
THE FREEZING DEPRESSION OF STABILIZED LATICES

Concentration of glycol (g./l.)	15	45	75
Depression in aqueous solution (°C)	0.46	1.46	2.54
Depression in stabilized AN.-latices (°C)	0.46	1.40	2.33
Depression in stabilized St.-latices (°C)	0.36	1.22	2.12

Table II shows that the St.-latex which is most easily stabilized has the lowest depression value and that the adsorption of glycol on emulsion particles has occurred in the St.-latices.

B) The Electrophoretic Mobility of Stabilized Latices.—The electrophoretic mobility of emulsion has been determined by the present researchers. As previously reported, it has been shown to alter by the adsorption of detergents. It is also suggested that the electrophoretic mobility changes by the adsorption of different solvents having different dielectric constants[2]. The partition of additives between the solution and the particles may be sensitive to the mobility. Thus the changes of mobility by stabilization are measured by the usual U-type assembly previously reported[3]. The results of the experiment are plotted in Figures 3 and 4.

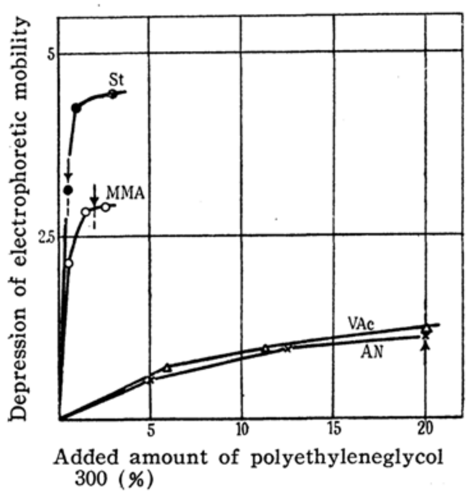

Fig. 3. The decrease of the electrophoretic mobility after the addition of ethyleneglycol (Emulsifier used was sodium dodecylsulfate 0.2%.).

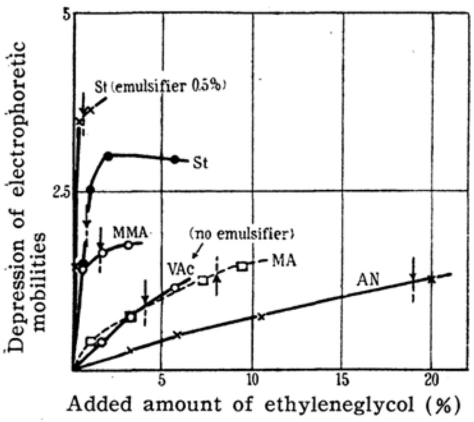

Fig. 4. The decrease of the electrophoretic mobility after the addition of polyethyleneglycol 300 (U. C. C. Ltd.) (Emulsifier used was sodium dodecylsulfate 0.2%).

As shown in Figs. 3 and 4, the order of the change of mobility is in good agreement with the order of the facility of stabilization. The stabilized points in each latex are marked with arrows which are in the neighbourhood of the saturation. The ratios of the mobilities of the stabilized latices to those of the originals are tabulated in Table III.

It is of interest to note that the average value of these ratios agrees with the ratio of dielectric constants of ethylene glycol and that of water, 41.2 (d.c. of glycol)/81.0 (d.c. of water) = 0.508.

C) The Adsorption of Additives on Emulsion Particles.—It is necessary to determine directly the amount of adsorption of additives for the investigation of freeze-thaw stability. Fortunately the concentration of ethyleneglycol and polyethyleneglycol in aqueous medium can be measured quantitatively by the periodic acid (volumetric) method[5], and by the Shaffer (gravimetric) method[4] respectively. Figure 5 gives the case of ethyleneglycol and Figure 6 that of polyethyleneglycol.

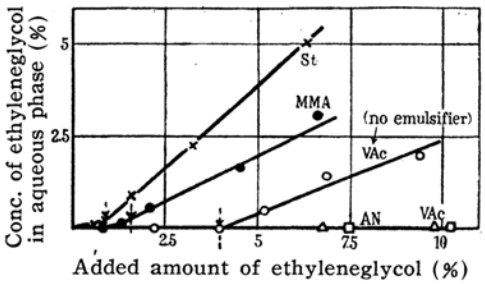

Fig. 5. The adsorption of ethyleneglycol on the emulsion particles (Arrows show points which have attained stability.). (emulsifier: Sodium dodecylsulfate 0.2%)

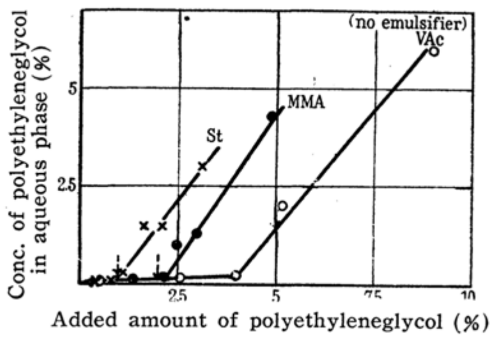

Fig. 6. The adsorption of polyethyleneglycol on the emulsion particles (Arrows show points which have attained stability.). (emulsifier: Sodium dodecylsulfate 0.2%)

TABLE III

RATIOS OF THE MOBILITIES OF THE STABILIZED AND UNSTABILIZED LATICES

Kind of Emulsion	St.	St.	MMA.	MA.	VAc.	AN	Average
Kind of Emulsifier	A	A	A	A	None	A	—
Conc. of Emulsifier	0.5	0.2	0.2	0.2	—	0.2	—
Ratio of Mobilities	0.49	0.67	0.58	0.57	0.59	0.48	0.56

2) E.K. Rideal, "An Introduction to Surface Chemistry," Camb., p. 406.

3) T. Motoyama and S. Okamura, *Mem. Fac. Eng. Kyoto Univ.*, 15, 242 (1653).

4) C.B. Shaffer and F.H. Critchfield, *Ind. Eng. Chem.*, 19, 32 (1947).

5) G.O. Curme and F. Johnston, "Glycols," Reinhold, (1952).

As represented in Figs. 5 and 6, the points of saturated adsorption coincide with the stabilizing points (shown as arrows in figures). Also the Figures indicate that the facility of saturated adsorption agrees with that of stabilization, (St.>MMA.>VAc.>AN.)

Summary

The freeze-thaw stability of synthetic latices obtained by the emulsion polymerisation of styrene, methyl methacrylate, methyl acrylate, vinyl acetate and acrylonitrile has been measured at the freeze-thaw cycles of $-17.5°C$ and room temperature. It is found that the addition of ethyleneglycol and polyethyleneglycol into the latices increases the stability. The freezing point depression and the electrophoretic mobility of stabilized latices indicate the adsorption of stabilizing additives on the emulsion particles. Finally the adsorption of ethylene glycol and polyethylene glycol on the emulsion particles is determined directly. In consideration of these experimental results the freeze-thaw stability seems to be attained by the adsorption of additives on the emulsion particles.

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