

Redispersible Latex Polymer

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Introduction

Synthetic latices formed by emulsion polymerization of one or more monomers are dispersions of polymer microspheres in an aqueous serum containing inorganic electrolytes and emulsifiers. The diameters of the latex particles may be more or less uniform and range in size from 0.03 to 0.5 μ , depending upon the composition of the latex and the method employed in its preparation. The particles in the dispersion are stabilized against coagulation by surface-active agents or protective colloids. Generally, most of the emulsion stabilizer is adsorbed on the surface of the latex particles and a very small amount is dissolved in the aqueous phase.

Synthetic latices have found extensive application in the formulation of various types of protective coatings. In most applications, the polymer particles must possess sufficient plasticity to permit their coalescence at the temperature of application upon removal of the water by evaporation. Since the presence of water in the latex adds to shipping costs, it is economically attractive to consider methods of producing latex polymers that contain a minimum amount of water. The ultimate limit for such a system would be a polymer which could be isolated completely from the aqueous medium in which it was formed and later redispersed at the time of use to re-form a latex for formulation and application.

Floria and Mock¹ described the preparation of latices formed by the copolymerization of styrene and sodium *p*-styrenesulfonate. These latices, after drying, were redispersible in water. However, no practical method was reported by which such redispersible systems could be utilized in coating applications.

Pateman² prepared emulsion copolymers of vinyl acetate and 2,2'-dichlorodiethyl maleate which could be readily dried to give a powder that could be reconstituted as an emulsion upon admixture with water. If either the original emulsion or a reconstituted emulsion were treated with an external plasticizer in an amount normally used in the plasticization of straight polyvinyl acetate, coherent flexible films were obtained. These plasticized films were not redispersible in water because of the fusion of particles upon drying the films.

In the course of preparing polymer latices of various compositions, we have discovered that certain other combinations of comonomers yield

latices which, after drying, can be re-formed upon the addition of water and a base.

Experimental

Latices exhibiting the property of redispersibility after drying can be prepared in a conventional manner with commonly known ingredients and surface-active agents. The essential feature appears to be the inclusion of relatively large amounts (greater than 10% by weight, based on total monomer weight) of a carboxylic comonomer, such as methacrylic acid. In our work, styrene and an acrylic ester comprised the balance of the monomeric mixture.

TABLE I
Polymerization Recipe

Ingredients	Parts, by weight
Styrene	55
2-Ethylhexyl acrylate	25
Methacrylic acid	20
Water	102
Sodium salt of an alkyl aryl sulfonate	2.55
Alkyl aryl polyether alcohol	0.50
Potassium sulfate	0.27
Potassium persulfate	0.40
Sodium pyrophosphate decahydrate	0.28

The polymerization reaction was carried out in a 2-l. resin flask equipped with heating mantle, reflux condenser, thermometer, agitator, and two dropping funnels. Latices were prepared by a continuous addition technique in 6 hrs. at a temperature of $90 \pm 2^\circ\text{C}$. Variations in polymer composition were made, as will be indicated, by changing the amounts of methacrylic acid and of 2-ethylhexyl acrylate in such a way as to maintain the total level of these ingredients at 45% of the total weight of monomers. Thus, the plasticity of the polymer changed somewhat as a function of its comonomer composition.

Particle size determinations were made from electron photomicrographs by a technique that will be described elsewhere.³

Results

Latices prepared according to the recipe given in Table I were spread, unneutralized, on glass plates and dried at ambient temperatures. The compositions to be described produced brittle crazed films because of their low plasticity. The polymers were easily removed from the substrate as granular free-flowing solids which could be stored in closed containers at room temperature for an indefinite period of time without discoloration or change in properties. Microscopic examination at $80\times$ revealed that this

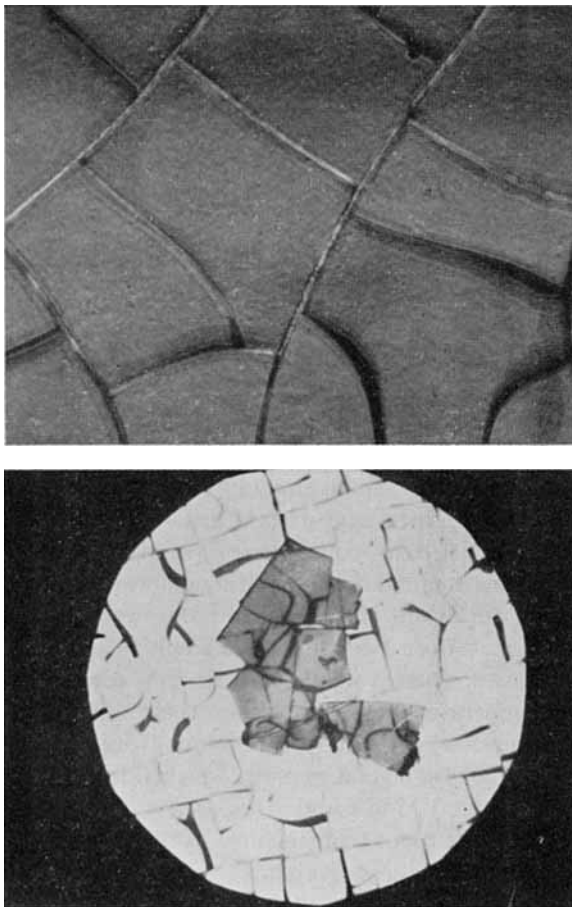


Fig. 1. Microscopic views of a dried latex film of 55/25/20 styrene/2-ethylhexyl acrylate/methacrylic acid terpolymer showing the transparent nature of the polymer granules.

material consisted of colorless transparent flakes, superficially crystalline in nature, as is shown in Figure 1.

No physical change was noted when this substance was added to water. However, the addition of an inorganic or organic base to the mixture to pH 9-10 produced an immediate peptizing action and a white liquid was formed which closely resembled the original latex prior to drying. If this alkaline latex was recast as a wet film on glass, the same type of crazed imperfect film resulted upon drying as that noted with the original acidic latex. Although the crazed film of the dried reconstituted latex was quite water-sensitive, it was not completely redispersible in water a second time. Baking the original or reconstituted polymer 30 min. at 150°C. rendered the material completely water-insensitive. Drying the original or reconstituted latex film at elevated temperatures resulted in the production of clear hard continuous films which were not water-sensitive.

TABLE II
Summary of Properties of High-Acid Latices
(55/(45 - X)/X styrene/ethylhexyl acrylate/methacrylic acid)

Properties of unneutralized latices	Acidic comonomer content (% by weight)						
	10	11	15	20	25	35	45
Continuous film @ RT	No	No	No	No	No	No	No
Redispersible	No	No	Yes	Yes	Yes	Yes	Yes
Thickening at pH 10	No	No	No	Yes	Yes	Yes	Yes
Calcium chloride stability	No	No	No	Yes	Yes	Yes	Yes
Alum stability	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Freeze-thaw stability	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Mechanical stability	Yes	Yes	Yes	Yes	Yes	Yes	Yes

As has been pointed out, these latex polymers are not film-formers without external plasticization. Small amounts (5-8% based on polymer solids) of a filming aid such as the glycols or Carbitol Acetate are sufficient to induce the formation of clear, continuous films at room temperature upon drying. A plasticized unbaked film, although water-sensitive, is not redispersible. The addition of 30 parts of a water-soluble melamine-formaldehyde resin (Super Beckamine, Reichold Chemicals, Inc.) to the original or reconstituted latex at pH 10.5 imparts coalescence to the films dried at room temperature. Upon baking, these films become extremely hard and are insensitive to water and common organic solvents. Even the addition of 20 parts of a solid resorcinol-formaldehyde resin (Penacolite B-16, Koppers Company, Inc.) under the same conditions produces clear and continuous films at room temperature. Catalytic quantities of amine are required in this case for crosslinking.

Variations in copolymer composition were made in an effort to define the limits within which water redispersibility could be expected. This work is summarized in Table II, in which certain other properties of these latices are tabulated.

The composition containing 45% methacrylic acid produced a viscous latex. Subsequent treatment with inorganic base produced an extremely viscous, clear solution. Others⁴ have reported this type of property for emulsion polymers containing high concentrations of carboxyl groups.

Several latices were prepared to assess the influence of polymer molecular weight and crosslinking on the redispersibility features of the polymer.

TABLE III
Particle Size Analysis of 55/25/20 Latex*

Sample	D_{vs}	D_n	D_n	D_{vs}/D_n	D_{vs}/D_n
Original	1280A.	920A.	830A.	1.39	1.54
Reconstituted	1370	1010	910	1.36	1.51

* $D_{vs} = \Sigma(nd^3)/\Sigma(nd^2) =$ Volume-to surface average diameter. $D_n = [\Sigma(nd^3)/\Sigma n]^{1/2} =$ Surface average diameter. $D_n = \Sigma(nd)/\Sigma n =$ Number-average diameter.

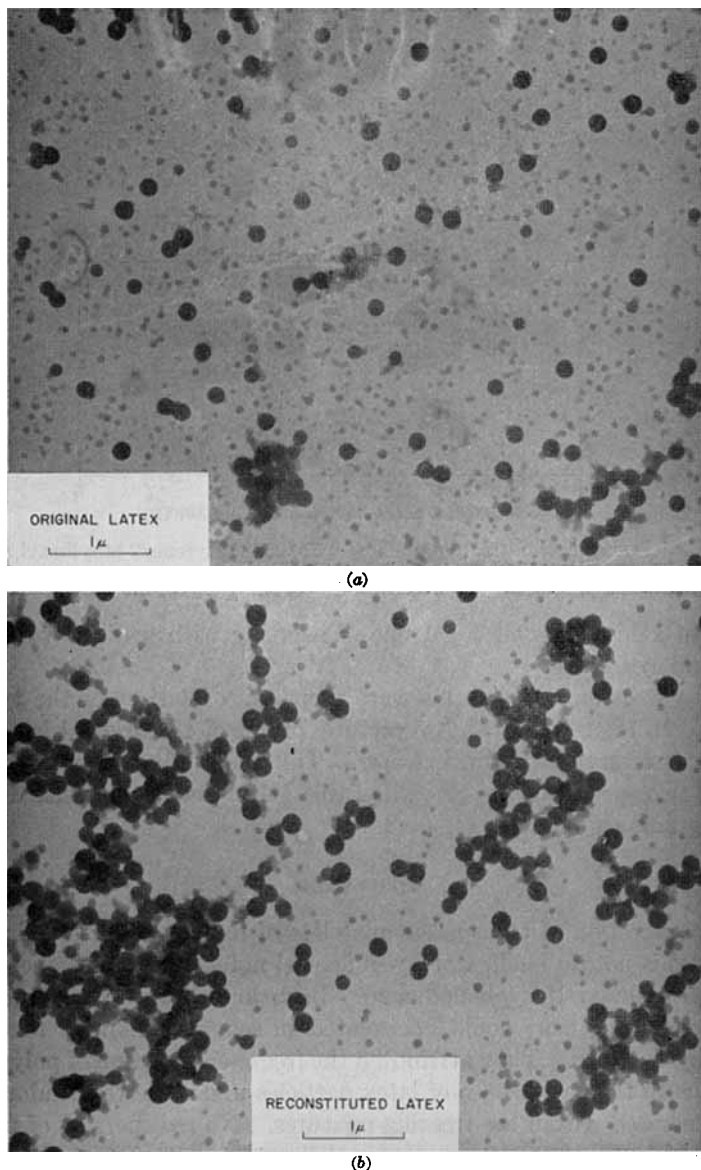


Fig. 2. Electron micrographs of a 55/25/20 styrene/2-ethylhexyl acrylate/methacrylic acid terpolymer latex before (a) and after (b) reconstituting with water and a base.

Copolymers of 55/25/20 styrene/ethylhexyl acrylate/methacrylic acid composition containing 0.25 and 1.0 part of tert-dodecyl mercaptan and 0.4 part of divinyl benzene (without mercaptan) displayed water-dispersibility features similar to compositions prepared without these ingredients. A latex containing 55 parts of styrene, 30 parts of butadiene, and 15 parts of methacrylic acid was prepared in a recipe similar to that given in Table I. This latex yielded a continuous film upon drying which was con-

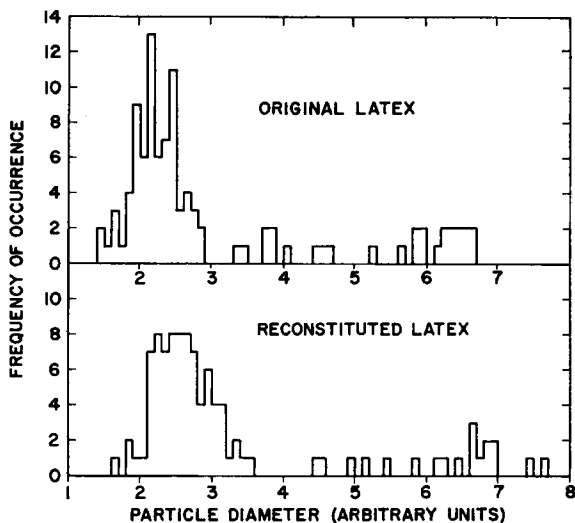


Fig. 3. Particle size distribution diagrams of a 55/25/20 styrene/2-ethylhexyl acrylate/methacrylic acid terpolymer latex before and after reconstituting with water and a base.

verted to a highly swollen gel upon rewetting with a dilute solution of potassium hydroxide.

Several electron micrographs were prepared of latices of the type described. In Figure 2 are shown pictures of one of the original latices and of the latex after redispersing in water. The results of particle size analyses of these two specimens are given in Table III. The particle size distribution diagrams are shown in Figure 3.

Discussion

The preparation of transparent platelets of rigid polymers by drying of latex films is not, in itself, worthy of special note. Many polymeric compositions undergo this phenomenon. Barb and Mikucki⁵ reported also that styrene polymers could be isolated in somewhat similar form from latices by freezing. They attributed the freeze-coagulation of polystyrene emulsions to the coalescence of latex particles under the tremendous pressures generated within the freezing mixtures. No redispersion of primary particles by any means was reported in their work.

The fact that a semiplastic water-dispersed polymer can be dried to a form which can be redispersed in water might be explained as a simple removal of water as from a slurry of glass beads. In the case described here, however, the dried granular polymer is a coarse grit of glistening particles superficially resembling a crystalline material. This is clearly suggested by microscopic examination, as shown in Figure 1. Although the latex particles are too small to be visible by means of an optical microscope, the transparency of the dried material strongly suggests that a degree of interparticle coalescence has occurred.

It has been shown⁶ that at 50,000 psi flat polymer surfaces will coalesce only very slowly below the second-order transition temperature. At the same pressure, rough-grained polymer powders can be made to interlock mechanically, but without any disappearance of the original grain boundaries. Thus, finely divided crystal polystyrene upon subjection to extreme pressures at ambient temperatures forms a white opaque pellet. Yet, as Figure 1 shows, the polymer fragments produced by simply drying a copolymer latex of the type described at a temperature considerably below the second-order transition temperature of the copolymer contained, are clear and transparent.

Although the latices herein described are not composed of unusually small particles, it seems likely that the interplay of forces upon drying might be such as to result in sufficiently large pressures being exerted on the particles as the water phase evaporates to cause particle coalescence. The capillary pressure exerted during the drying process on a system of spheres 0.1 μ in diameter has been calculated by Brown to approximate 80 atm. in its magnitude.⁷ This, coupled with surface forces in a drying film, could result in a compressive force of considerable magnitude. Although the temperature of the system is below the second-order transition temperature of the polymer (minimum film-forming temperatures above 88°C. have been observed), the particles evidently possess sufficient plasticity to permit some deformation upon drying. Plasticization by water, which occurs to some extent, probably contributes to this effect. Cross-linking from the inclusion of small amounts of divinyl benzene does not increase the polymer modulus sufficiently in the systems studied to influence significantly the filming properties.

The polar forces arising from the presence on the particle surfaces of carboxyl groups and adsorbed surfactant molecules tend also to limit particle coalescence. Although Figure 1 suggests that sufficient coalescence has occurred to destroy grain boundaries, Figure 2 and the particle size averages cited in Figure 3 and Table III comprise convincing evidence that the original particles are restored upon recontact with water. It is perhaps surprising that the particles after redispersion are clearly spherical in shape. This is another indication of the semiplastic nature of the polymer and the magnitude of surface forces which, upon redispersion of the polymer in water, tend to restore the particles to sphericity.

Since surfactant molecules are attached to the particle surfaces by physical adsorption, they are somewhat mobile and would tend to be displaced to some degree during film drying. Addition of water to the polymer grit leaches surfactant from the exposed surfaces. This is probably the reason that no peptizing action by water is observed until base is added. The presence of a base causes ionization of the carboxyl groups attached to the particles. The sudden development of large repulsive Coulombic forces causes the separation of individual latex particles from the polymer matrix, enabling surface forces to restore the particles to their original spherical shape. The rapidity with which this occurs suggests that a con-

siderable portion of the acid groups in the polymer is concentrated at the particle interface.

If it is assumed that all of the carboxyl groups are distributed evenly over the particle surfaces in a 1000-Å particle size latex containing 20 parts of methacrylic acid, it can be shown that there is one carboxyl group for each 4–5 Å.² of surface area. Obviously, this is a much higher surface density of carboxyl groups than is physically possible. The calculation, therefore, shows that there are sufficient carboxyl groups present to permit fairly high surface concentrations. Because of the polarity of the acid groupings, it is reasonable to expect that they would tend to concentrate near the polymer–water interface.

The data in Table II indicate that methacrylic acid in excess of 11% by weight is required to cause redispersion. Even at this level, there is more than a sufficient number of acidic groups present to accommodate close packing on the particle surface. Since it is difficult to visualize how polar groups within the particle could influence the tendency of the particles to become redispersed in water upon raising of the pH, it is concluded that, because of the distribution of acid groups inside and on the particles, amounts greater than 11% of methacrylic acid are required in order to produce sufficient surface polarity that spontaneous rehydration and dispersion of the particles is possible.

Apparently, no upper limit exists to the amount of acidic groups necessary for redispersion in the type of system we have studied. At very high carboxyl contents, the solubilizing effect of the carboxylate ions is sufficient to cause destruction of the particle shape, converting the system to a colloidal solution.⁴

We have no adequate explanation of the fact that these systems are not amenable to redispersion a second time or more. It may be that carboxyl groups are redistributed by molecular motion in the particle upon drying so they are not available for hydration a second time. Possibly, under the pressures developed in the drying process, acid groups are forced into the particle and thus inactivated. The fact that heating the dry granules of the original latex for 3 hr. at 100°C. destroys the redispersibility feature may indicate that sufficient polymer flow has occurred to disrupt the particle interfaces. A small amount of divinyl benzene was included in one preparation to determine whether increased rigidity and decreased molecular mobility in the polymer particle would prevent the apparent loss of exposed carboxyl groups by this means and permit redispersion a second time: no effect of this type was observed.

In other experiments, a molecular-weight modifier was introduced to determine whether a change in particle plasticity for a given composition would influence the susceptibility of the particles to hydration and redispersion: no change was noted. However, the addition of 5–8% of a filming aid leads to sufficient plasticization that complete coalescence results and a continuous film is formed. These additives probably also lubricate the particles which facilitates their movement upon drying and relieves me-

chanical stresses. It is probable that latex polymers containing sufficient acrylic ester to permit formation of a continuous film would not be redispersible. This is a likely reason for the absence of the redispersibility feature in the styrene/butadiene/methacrylic acid latex referred to earlier.

References

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Synopsis

Latices containing 55 parts of styrene, $(45 - X)$ parts of 2-ethylhexyl acrylate, and X parts of methacrylic acid, where $X \geq 15$, have been shown to yield discontinuous crazed films upon drying. These clear transparent polymer granules upon immersion in water containing a base are peptized to form a reconstituted latex containing spherical particles of the same size as the original latex particles. Inclusion of small amounts of a filming aid in the original or reconstituted latex permits the deposition of continuous polymer films which are rendered water-resistant by baking. The property of redispersibility in water of transparent flakes of polymer is attributed to limited particle coalescence in the polymer grit. The incorporation of relatively high levels of carboxyl groups in the polymer is essential to the redispersion of the polymer by dilute solutions of base. Ionization of the carboxyl groups on the particle surfaces upon addition of a base gives rise to the sudden development of repulsive Coulombic forces which cause particle separation, after which surface forces are sufficient to restore the semiplastic particles to their original spherical shape. Inability to redisperse the film a second time may be due to polymer plasticization or to the migration of carboxyl groups to the particle interior as a result of coalescence forces.

Résumé

On a démontré que le séchage de réseaux contenant 55 parties de styrène $(45 - X)$ parties d'acrylate de 2-éthylhexyle et X parties d'acide méthacrylique $(X \geq 15)$, produit des films discontinus et fissurés. Ces granules clairs et transparents de polymères sont peptisés par immersion dans une solution aqueuse basique et forment ainsi un latex reconstitué contenant des particules sphériques de la même grandeur que celles du latex original. L'inclusion de petites quantités d'un agent aidant la formation de films dans le latex original ou reconstitué permet la formation de films continus de polymère, qui sont rendus résistants à l'eau par cuisson. La propriété de redispersabilité dans l'eau de flocons transparents de polymère est attribuée à la coalescence limitée des particules de polymères. L'incorporation de teneurs relativement élevées de groupes carboxyliques dans le polymère est essentielle à la redispersion du polymère dans les solutions diluées d'une base. L'addition de la base cause une ionisation des groupements carboxyliques à la surface des particules; l'augmentation des forces carboxyliques de répulsion mène à la séparation des particules, après quoi la tension superficielle suffit pour rendre aux particules semi-plastiques leur forme sphérique originale. L'inaptitude de redisperser le film une seconde fois est peut-être due à la plastification du polymère ou à la migration de groupes carboxyliques vers l'intérieur des particules par suite des forces de coalescence.

Zusammenfassung

Latices mit 55 Teilen Styrol, $(45 - X)$ Teilen 2-Athylhexylacrylat und X Teilen Methacrylsäure, wo $X \geq 15$, liefern beim Trocknen diskontinuierlich, rissbildende Filme. Die klaren, transparenten Polymerkörnchen werden beim Einbringen in eine wässrige Base peptisiert und bilden wieder einen Latex mit kugelförmigen Teilchen derselben Grösse wie die ursprünglichen Latexteilchen. Zusatz kleiner Mengen eines Filmbildungsmittels zum ursprünglichen oder rückgebildeten Latex erlaubt die Gewinnung eines kontinuierlichen Polymerfilms, der durch Erwärmen wasserbeständig gemacht werden kann. Die Fähigkeit transparenter Polymerflocken zur Redispersierung in Wasser wird auf eine begrenzte Teilchenkoaleszenz im Polymeren zurückgeführt. Für die Redispersierung des Polymeren in verdünnten Basenlösungen ist der Einbau eines verhältnismässig grossen Anteils von Karboxylgruppen in das Polymere notwendig. Ionisation der Karboxylgruppen an der Teilchenoberfläche beim Zusatz von Basen führt zur plötzlichen Entwicklung Coulombscher Abstossungskräfte und Teilchentrennung; nun genügen die Oberflächenkräfte, um die ursprüngliche Kugelgestalt der halbplastischen Teilchen wider hersuzustellen. Die Unfähigkeit den Film ein zweites Mal zu redispersieren kann auf eine Weichmachung des Polymeren oder auf die Wanderung von Karboxylgruppen ins Teilcheninnere unter dem Einfluss der Koaleszenzkräfte zurückzuführen sein.

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