Formation of Films by Drying of Latex

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Synopsis

A new theory to help explain the mechanism of latex film formation is advanced. The essential features of this theory are that: (1) the major energy source for film formation is the heat of the surroundings; this heat is converted to useful (film-forming) work by evaporation of the water; the incipient and nascent film is the engine; (2) an important mechanism whereby evaporation of the water does useful work is by diffusion of water through the polymer particles themselves. The contributions of capillarity and wet sintering to the film forming process are analyzed and are found to be of greatest importance during the first half or so of the particle coalescence process. Experimental evidence supporting the above picture is presented.

INTRODUCTION

The formation of a continuous film by the evaporation of water from an aqueous dispersion of plastic polymeric particles is a phenomenon of considerable practical importance for such items as latex paints, paper coatings, and latex adhesives. The mechanisms which have been proposed for this phenomenon, however, have been less than satisfactory in explaining all the observations.

The first attempts to provide a rationale for this phenomenon are due to Dillon et al.[1] Essentially, these workers proposed that, after evaporation of the water, the dry latex particles fuse together under the impetus of the force resulting from the sharp angle of contact between the particles and the surface free energy of the polymer–air interface. This mechanism will be referred to as dry sintering.

Later, Brown[2] proposed that the primary force giving rise to particle coalescence is the capillary pressure due to curvature of the air–water interface in the void areas in the surface of the film.

Recently, Vanderhoff et al.[3] have analyzed theoretically the process involved when the flocculated particles coalesce while immersed in water. This process is completely analogous to the dry sintering process, except that the driving force is the free energy of the polymer–water interface. This process will be referred to as wet sintering.

In this paper the contributions of the above mechanisms to the film-forming process are analyzed, a new mechanism is proposed, and a general description of the overall film-forming process is set forth.

Some experiments aimed at elucidating the film-forming process are also described.

EXPERIMENTAL

Rate of Drying of Latex Film

One of the most serious problems in determining rates of drying is the tendency of a film cast on a flat plate to dry from the perimeter in. Moreover, the rate of drying, especially during the early part of the process when the surface is essentially pure water, is very dependent on the rate at which heat is transferred into the system and the rate at which water vapor is transported away from the surface. To get comparative rates, one is thus obliged to run the two samples side by side under identical conditions rather than sequentially.

It was found that the most consistent results were obtained by saturating 45 × 45 mm. swatches of ordinary blotting paper with latex, laying the paper on a 50 × 50 × 2 mm. glass plate, fastening down the edges of the blotting paper with thin wire to prevent curling, and weighing the whole assembly at regular intervals. The use of the blotting paper circumvented the problem of nonuniform drying and obviated the necessity of keeping the sample precisely level. Thus, a number of samples could be dried simultaneously side by side under essentially identical conditions of temperature, relative humidity, air circulation, etc.

The latexes for this study were prepared by using 2-sulfoethyl methacrylate sodium salt (SEM⁻Na⁺) as comonomeric emulsifier according to the general procedure described earlier.[4] This technique yields latexes in which sulfonate groups are irreversibly attached to the particle surfaces. Such latexes may be exhaustively dialyzed without coagulation.

These polymerizations were deliberately conducted so as to make the latexes as identical as possible save for copolymer composition. The properties of the raw latexes are tabulated in Table I.

Samples of these latexes were placed in ⁵/₈-in. diameter regenerated cellulose dialysis tubing and exhaustively dialyzed (2 weeks) against flowing deionized water. The density and solids data for the samples used in this study are tabulated in Table II.

TABLE I

Copolymer[a]	Emulsifier	Solids, %	Particle diameter (light scattering), A.
70/30 VeCl$_2$/n-BA	1% SEM⁻Na⁺	54.4	1500
67/33 EA/MMA	1% SEM⁻Na⁺	52.6	1600

[a] VeCl$_2$ = vinylidene chloride; n-BA = n-butyl acrylate; EA = ethyl acrylate; MMA = methyl methacrylate.

TABLE II

| | Latex density, | Latex solids, % | |
Latex composition	g./cc.	By weight	By volume
70/30 VeCl₂/n-BA	1.1115	32.5	27.8
67/33 EA/MMA	1.035	24.7	25.2

In Figure 1 the percentage polymer by volume is plotted as a function of drying time for these latexes. This shows that the ethyl acrylate–methyl methacrylate (EA/MMA) copolymer latex dries more rapidly than does the vinylidene chloride–n-butyl acrylate (VelCl₂/n-BA) copolymer one. The differences in drying rate appear only at higher solids. This experiment was repeated four times, and each time substantially the same relative rates were obtained.
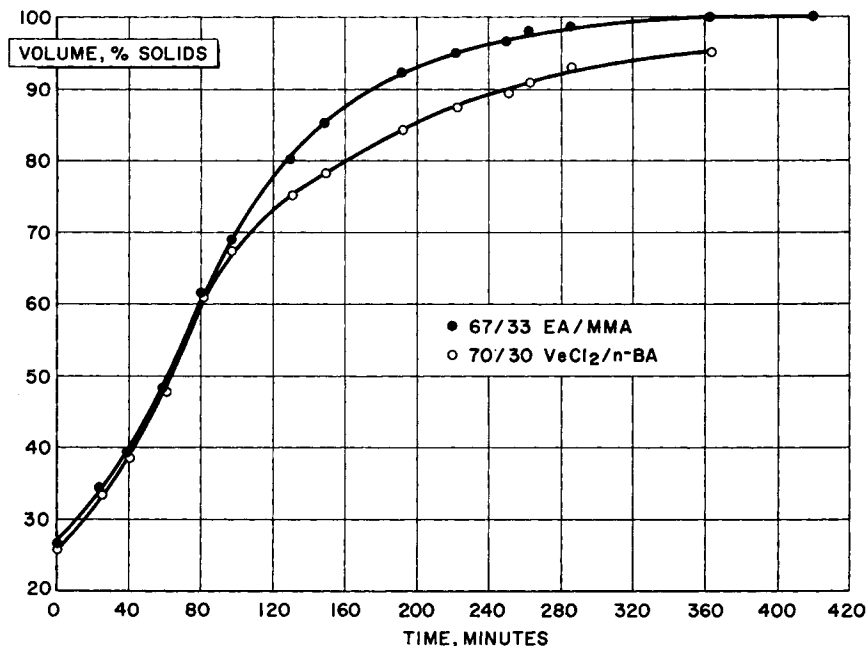

Fig. 1. Rate of evaporation at 24°C., 24% R.H.

Degree of Coalescence Due to Wet Sintering

A $^{60}/_{40}$ MMA/BA copolymer latex was prepared by using 2-aminoethyl methacrylate·HCl (AEM·HCl) as comonomeric emulsifier according to the general method described by LeFevre and Sheetz.[5] This latex, which contained cationic groups irreversibly attached to the particle surfaces, was placed in a $^{5}/_{8}$-in. diameter regenerated dialysis sack and exhaustively dialyzed (2 weeks) against flowing deionized water. The properties and composition of this latex are shown in Table III.

TABLE III

Composition	Emulsifier	Particle diameter (light scattering), A.	Solids (after dialysis), %	Polymer density, g./cc.	Minimum film formation temperature (MFT), °C.
60/40 MMA/n-BA	AEM·HCl, 0.70% (on polymer)	1750	49.7	1.13	32–34

A sample of the dialyzed latex in a $^5/_8$-in. diameter regenerated cellulose dialysis bag was immersed in aqueous $0.072M$ dialyzed poly-AEM·HCl at about 5°C. for 18 hr. Under the influence of osmotic pressure (about 0.2 atm.) water diffused out of the latex to yield an agglomerate of essentially undistorted polymer particles, the interstitial portions of which were filled with water. After removal from the dialysis bag, samples of this agglomerate were placed in deionized water and maintained for 2 hr. at 36°C. and for 2 hr. at 36°C. plus 2 hr. at 50°C., respectively. Solids content in the samples were determined gravimetrically. The results obtained are presented in Table IV.

TABLE IV
Effect of Heating on Agglomerate Solids

	Solids (by vol.), %
Initial agglomerate	62.3
Agglomerate after 2 hr. at 36°C.	84.8
Agglomerate after 2 hr. at 36°C. + 2 hr. at 50°C.	87.2

In order to assess the effect of adsorbed surfactant on the degree of wet sintering, a sample of the initial agglomerate (15 g.) was heated for 1 hr. at 26°C. in deionized water and immersed in 100 ml. of 1% aqueous Dowfax 9N15 (the adduct of 15 moles of ethylene oxide per mole of nonylphenol) for 14 days at 5°C. (The heating at 26°C. did not affect the solids content appreciably, but it was necessary to fuse the particles sufficiently so that the agglomerate did not spontaneously redisperse in the Dowfax solution.) A sample of the agglomerate obtained was heated for 2 hr. at 36°C. in 1% aqueous Dowfax 9N15. The solids content of the agglomerate before and after heating at 36°C. was 61.8 and 66.2 vol.-%, respectively.

Drying of Latex Under a Water-Permeable Film

A $^{65}/_{35}$ MMA/n-BA latex (50% solids) prepared with the use of 0.70% AEM·HCl as comonomeric emulsifier[5] was cast as a film 0.015 in. thick on a glass plate. A portion of this wet film was covered directly with a

$^{95}/_5$ MMA/n-BA copolymer film 0.0007 in. thick. Another portion of the same wet latex film was covered with the same $^{95}/_5$ MMA/n-BA film, but with the difference that an air gap was maintained between the two films. Thus, both films dried at essentially the same rate. After drying (10 hr.) at about 24°C. the latex film covered directly with the $^{95}/_5$ MMA/n-BA film was continuous and clear, whereas the latex film dried with air in contact with the surface was cloudy and discontinuous.

DISCUSSION

Analysis of Previous Theories

The Dry Sintering Theory. As has been adequately pointed out by Brown,[2] the dry sintering mechanism is inconsistent with the observation that film formation and water evaporation are concurrent events. Serious consideration of this mechanism, therefore, seems unnecessary.

The Capillary Theory. In developing the quantitative aspects of this theory, Brown[2] considers the model shown in Figure 2, in which the pore size in the surface of the film is approximated by considering it to be that of the enclosed small circle (radius r_c). It can be shown that

$$r/(r + r_c) = \cos 30° \tag{1}$$

and therefore $r_c = 0.155r$.

The compressive pressure due to the curvature of the water in the surface of this capillary is given by the Young-Laplace equation and is

$$P_c = 2\gamma_{H_2O/a}/r_c = 12.9\gamma_{H_2O/a}/r \tag{2}$$

where $\gamma_{H_2O/a}$ is the surface tension of the air–water interface.

Brown has calculated P_c as a function of r assuming $\gamma_{H_2O/a}$ to be 30 dynes/cm. His results are tabulated in Table V.

TABLE V
Pressure and Particle Size for $\gamma_{H_2O/a}$ = 30 dynes/cm.

Particle diameter, μ	Pressure, kg./cm.^{2}
1.0	7.9
0.1	7.9×10^1
0.01	7.9×10^2
0.001	7.9×10^3

It is interesting to note that the tenacity of pure water has been reported[6,7] to be on the order of 40 kg./cm.^{2}. This means that the maximum P_c attainable will be no more than 40 kg./cm.^{2}, eq. (2) notwithstanding. Indeed, it would not be surprising to find that an aqueous colloid such as a latex might have a tensile strength much less than that of pure water. Hence, the maximum compressive pressure may be much less than predicted by eq. (2).
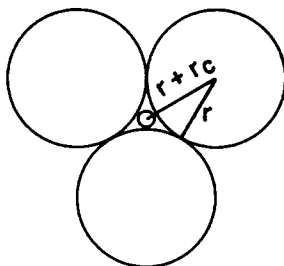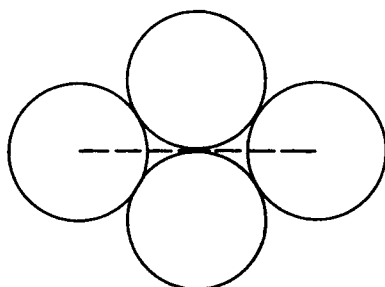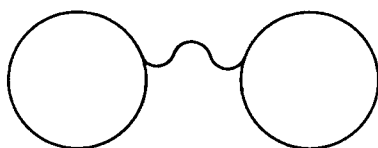
Figure 2.

Figure 3.

Figure 4.

In the following discussion I shall borrow the simplifying assumption of Brown and consider the water interface in the "throat" between three mutually touching spheres in the surface layer to be equivalent to that in a capillary of radius r_c.   Rather than regard the effect of capillarity in terms of a general pressure P_c, I shall examine the compressive contribution of the water–air interface in each surface hole in terms of components, G_n and G_p, normal to and parallel to the surface, respectively. G_n, the normal force, can be considered as a vector quantity, but G_p, the force parallel to the surface, is the total force exerted around the perimeter of the surface hole directed toward the center and is therefore polydirectional.

Figure 3 shows the view from the top down onto a portion of the surface of close-packed uniform spherical particles, and Figure 4 gives the view of the water–air interface, when the layer of spheres is half immersed, along the plane normal to the surface shown by the dotted line in Figure 3. Although Brown does not mention the subject, a contact angle θ of zero between polymer and water is implicit in his treatment.   This is seldom
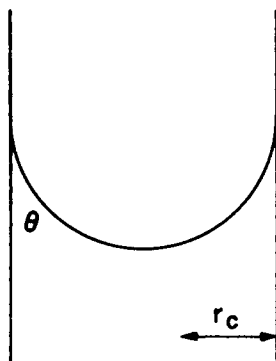
Figure 5.

the case with real latexes—as will be shown later—and therefore θ will be considered in deriving G_n and G_p.

Figure 5 shows the water–air interface in a longitudinally bisected capillary of radius r_c and contact angle θ between water and capillary (polymer). The forces exerted by the water–air interface can be calculated by considering the surface tension to be the mechanical equivalent of an elastic skin which exerts a tension of $\gamma_{H_2O/a}$ dynes/cm. It follows that the force exerted by the elastic skin downward on the capillary wall, G_n, must be $2\pi r_c \gamma_{H_2O/a} \cos \theta$. This combined with eq. (1) gives

$$G_n = 2\pi(0.155r)\gamma_{H_2O/a} \cos \theta$$

$$= 0.975r\gamma_{H_2O/a} \cos \theta \qquad (3)$$

In terms of pressure exerted on the cross-sectional area of the capillary, πr_c^2, this then becomes

$$P_n = \frac{0.975r\gamma_{H_2O/a} \cos \theta}{\pi r_c^2} = \frac{0.975\gamma_{H_2O/a} \cos \theta}{\pi(0.115)^2 r} = \frac{12.9\gamma_{H_2O/a} \cos \theta}{r} \qquad (4)$$

When $\theta = 0$, $\cos \theta = 1$ and P_n is then equivalent to Brown's P_c.

Referring to Figure 5, it is apparent that the force exerted by the "elastic skin" tending to pull the walls of the capillary toward the center must be

$$G_p = 2\pi r_c \gamma_{H_2O/a} \sin \theta$$

and from eq. (1),

$$G_p = 0.975r\gamma_{H_2O/a} \sin \theta \qquad (5)$$

From eqs. (3) and (5) it follows that at zero contact angle G_n, the force per hole exerted by the air–water interface normal to the surface, is maximum whereas G_p, the component parallel to the surface, is zero. As θ increases, however, G_n gets smaller and G_p bigger; at $\theta = 45°$, $G_n = G_p$, and at $\theta = 90°$, $G_n = 0$ and $G_p = 0.975r\gamma_{H_2O/a}$. Thus, the action of the capillary force on the film surface is very much dependent on the magnitude of the contact angle, θ.
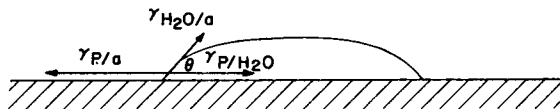
Figure 6.

As was mentioned earlier, θ is probably seldom zero in real latex systems. Figure 6 shows a drop of water in contact with a flat surface of polymer where $\gamma_{P/a}$, $\gamma_{H_2O/a}$, and γ_{P/H_2O} refer to the surface tensions, respectively, of the polymer–air, water–air, and polymer–water interfaces. From this the Young equation can be deduced,

$$\gamma_{P/a} = \gamma_{P/H_2O} + \gamma_{H_2O/a} \cos \theta \tag{6}$$

from which follows the condition that when $\theta = 0$,

$$\gamma_{P/a} \rightleftharpoons \gamma_{P/H_2O} + \gamma_{H_2O/a} \tag{7}$$

Now for most organic polymers $\gamma_{P/a}$ is probably in the range of 20–40 dynes/cm., and γ_{P/H_2O} can be considered to lie somewhere in the range 0–20 dynes/cm. In the presence of the surface active agents, etc., which must be present in a latex to effect stabilization, γ_{P/H_2O} is probably on the order of 0–10 dynes/cm. $\gamma_{H_2O/a}$ for essentially all latexes lies in the range of 30–70 dynes/cm. Calculation of θ, by using eq. (6) and arbitrarily chosen values of $\gamma_{P/a}$, $\gamma_{H_2O/a}$, and γ_{P/H_2O} in the ranges defined above shows that θ is often greater than 45°. This means that G_p is often greater than G_n.

If one considers any particular latex, one can, theoretically at least, change $\gamma_{H_2O/a}$ over a range of from about 30 dynes/cm. to about 60 dynes/cm. by removing or adding surfactant. In doing so γ_{P/H_2O} will of course also be changed but much less dramatically, since the maximum γ_{P/H_2O} attainable is probably no more than about 10 dynes/cm. Likewise $\gamma_{P/a}$ may also be affected, but again probably not to any great degree, since the lipophilic portion of the surfactant which will tend to orient toward the air will have about the same surface energy as the polymer itself.

Let it be assumed then that, on changing the surfactant concentration in a particular latex, $\gamma_{P/a}$ and γ_{P/H_2O} remain constant. It will also be assumed that θ becomes zero when $\gamma_{H_2O/a}$ reaches 30 dynes/cm. and, hence, from eq. (6) $\gamma_{P/a} - \gamma_{H_2O/P} = 30$.
Combining this with eq. (6) we obtain

$$\cos \theta = 30/\gamma_{H_2O/a} \tag{8}$$

Substituting this result in eq. (3) we see that

$$G_n = (0.975)(30)r = 29.2r \tag{9}$$

which means that the capillary force normal to the surface is independent of $\gamma_{H_2O/a}$.

By using the same assumptions and combining eq. (8) with eq. (5) by means of the trigonometric relationship

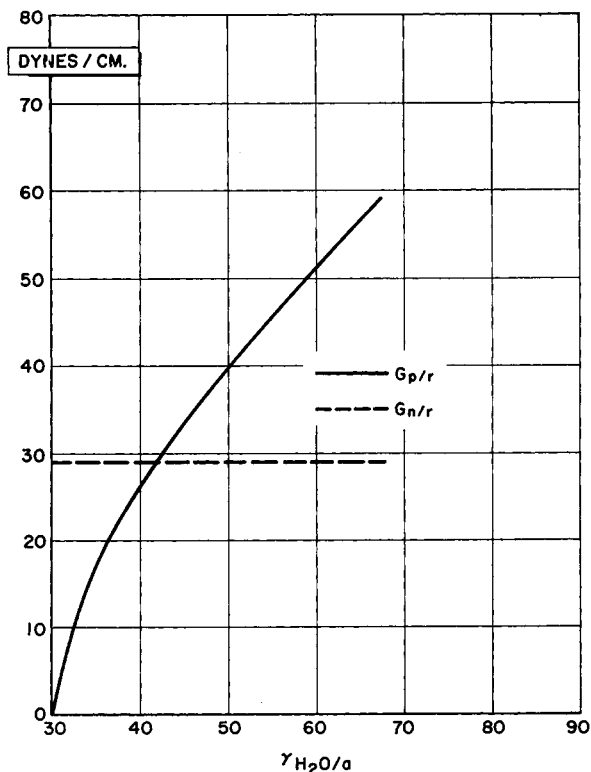$$\cos^2 \theta + \sin^2 \theta = 1$$

Fig. 7. Calculated effect of $\gamma_{H_2O/a}$ on G_p/r and G_n/r.

it is seen that

$$G_p = [0.975(\gamma^2_{H_2O/a} - 900)^{1/2}]r \tag{10}$$

In Figure 7 G_p/r, calculated by using eq. (10), is plotted as a function of $\gamma_{H_2O/a}$. The dotted line is G_n/r. It is seen that the net result on the capillary force of increasing $\gamma_{H_2O/a}$ is not to increase the compression normal to the surface but rather to increase the force tending to seal the surface over with polymer. This is in contrast to Brown's conclusion, eq. (2), that the compressive pressure varies directly with $\gamma_{H_2O/a}$.

The derivation of G_n and G_p is based on a model in which it is assumed that the hexagonally close-packed spheres in the surface layer are not deformed. However, in a film-forming latex deformation of the particles does occur and consequently, the surface holes shrink. The rate of this shrinkage relative to the rate of overall compaction will be some direct function of the ratio G_p/G_n. At $\theta = 0$, $G_p/G_n = 0$, but, when $\theta > 0$, G_p/G_n will increase with increasing $\gamma_{H_2O/a}$. However, even if $\theta = 0$, distortion of the surface particles by G_n will result in shrinkage of the surface holes.

As the surface holes shrink, the radius of curvature of the water interface in each surface hole decreases. An increase in compressive pressure would
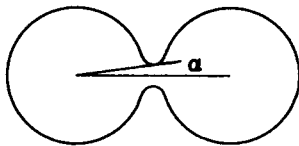
Figure 8.

therefore be predicted with the practical limit being the tensile strength of the system. However, the overall rate of water evaporation from the air–water interface will be reduced as the total air–water interface shrinks. In addition, the Kelvin equation,

$$\ln P/P_0 = -2\gamma_{H_2O/a}V/rRT \tag{11}$$

where r is the radius of curvature, V is the molar volume, P_0 is the normal vapor pressure, P the vapor pressure in the curved interface, T the absolute temperature, and R the gas constant, predicts that the vapor pressure of the water in the interface will decrease with decreasing r. Moreover, Shereshefsky and Carter[8] have found that the vapor pressure of water in capillaries of 3–10 μ radius was 80–10 times less, respectively, than that predicted by the Kelvin equation. That is, the deviation from the Kelvin equation became greater at smaller radii, and at a radius of 3μ the reduction of vapor pressure was already 80 times greater than predicted by the Kelvin equation. It seems reasonable to expect then that the vapor pressure of the water in the holes in the surface of the film (less than 0.1 μ radius) will be far less than the normal vapor pressure. Since the rate of evaporation is a function of the vapor pressure of the liquid at the interface, this means that the rate of water evaporation per unit area of water surface will decrease markedly as the surface holes shrink.

Taken together the foregoing considerations lead to the conclusion that the rate of water evaporation from the drying latex film should become exceedingly slow during the later stages of the drying process. This conclusion is not supported experimentally. The rate of water evaporation becomes slower above about 70% solids but not to the extent which might be expected where the only route of egress for the water the air–water interface. Moreover, a $^{67}/_{33}$ EA/MMA copolymer latex dries at a faster rate than does an analogous $^{70}/_{30}$ VeCl$_2$/n-BA copolymer one.

These considerations suggest that the water is leaving the film by some other route in addition to the air–water interface.

The Wet Sintering Theory. Vanderhoff et al.[3] have calculated the pressure tending to push two spheres together as a function of the degree of coalescence measured by the angle α (Fig. 8). Assuming that both radii of curvature describing the surface at the narrowest portion vary with coalescence, they find that very high pressures are generated at very low values of α, but that these tend to become negligibly small as α approaches 30°. If this model is correct, it follows that the wet sintering mechanism

cannot be invoked to explain the coalescence effected toward the end of the compaction process.

The experimental results support this conclusion. With the latex containing relatively little surfactant (high γ_{P/H_2O}) wet sintering caused the agglomerate to compact to 84.8 vol.-% solids at 36°C., 2°C. above MFT. Even at 50°C. the agglomerate solids only increased to 87.2%. Thus, wet sintering was incapable of completely compacting the agglomerate. Moreover, in the presence of excess nonionic surfactant (low γ_{P/H_2O}) the role of wet sintering was appreciably reduced; the solids of the agglomerate increased only to 66.2% at 36°C. As ordinarily used, latexes contain an excess of surfactant over that needed to cover the surface with one monolayer. These results indicate that wet sintering, therefore, usually plays no more than a minor role in the film-forming process and also that that role is confined to the early stages of the coalescence process.

THERMODYNAMICS

Whatever the forces are tending to fuse the particles together and from whatever mechanism they arise, it is axiomatic that the process is one involving conversion of energy to useful (film-forming) work.

It is immediately evident that the energy source for the dry sintering mechanism is the surface free energy of the air–polymer interface, $\Delta F_s^{P/a}$, which automatically becomes available as the particles fuse together. Analogously, the surface free energy of the polymer-water interface, $\Delta F_s^{P/H_2O}$, is the energy source for the wet sintering process.

Brown[2] implies that $\Delta F_s^{P/H_2O}$ also is the energy source for the fusion process via the capillary mechanism. However, the mechanism whereby this energy (which is released on coalescence of the interior latex particles) is transferred to the water–air interfaces in the surface of the film is not discussed.

Latex films ordinarily dry under more or less isothermal conditions. That is, the drying process takes up heat from the surroundings. Only a fraction of this heat which is taken up to evaporate the water, however, is available to do film-forming work. The available portion is the PdV work the water can do when evaporated isothermally and reversibly. This is the Gibbs free energy change, ΔF_e, for the evaporation process.

In order to get some idea of the relative magnitudes of $\Delta F_s^{P/a}$, $\Delta F_s^{P/H_2O}$, and ΔF_e, these quantities for the film-forming process at 25°C. and 0% R.H. have been calculated using as a model a sample of latex containing uniform particles in such concentration that a maximum packing has just been achieved. The properties of this hypothetical sample are: weight, 10.0 g.; density, 1.00 g./cc.; particle diamater, 0.2 μ; solids 75%; with

$$\gamma_{P/a}\ 30\ \text{ergs/cm.}^2$$

$$\gamma_{P/H_2O}\ 5\ \text{ergs/cm.}^2$$

$$\Delta F_s{}^{P/a} = (\Delta \text{ surface area}) \ (\gamma_{P/a})$$
$$= (\text{area per particle}) \ (\text{no. of particles}) \ (\gamma_{P/a})$$
$$= (4\pi r^2) \ (7.5/{}^4/_3\pi r^3) \ \gamma_{P/a}$$
$$= (22.5/r) \ (\gamma_{P/a}) = 0.675 \times 10^8 \text{ ergs} = 1.61 \text{ cal.}$$

$$\Delta F_s{}^{P/H_2O} = (\Delta \text{ surface area}) \ (\gamma_{P/H_2O})$$
$$= 0.27 \text{ cal.}$$

$$\Delta F_e = (\text{vapor pressure of } H_2O) \ (\text{Vol. of 2.5 g. saturated } H_2O \text{ vapor})$$
$$= (23.756/760 \text{ atm.}) \ (109 \text{ l.}) = 3.4 \text{ l.-atm.} = 82.3 \text{ cal.}$$

In order to get some idea of the amounts of energy required for the formation of the film, the work involved in compressing 10 cc. of the latex described above to solid polymer (7.5 cc.) has been calculated for the three following hypothetical conditions: (*1*) constant pressure of 10 atm.; (*2*) $P = K\Delta V^2$, $P = 100$ atm. when $\Delta V = 2.5$ cc.; (*3*) $P = K'\Delta V^3$, $P = 100$ atm. when $\Delta V = 2.5$ cc.

In (*1*), the unrealistic situation of the polymer resisting with a constant pressure is assumed. In (*2*) and (*3*) the polymer resists more as the compression increases.

The amounts of work involved for conditions (*1*), (*2*), and (*3*) are calculated in eqs. (12), (13), and (14), respectively.

$$w = P\Delta V = (10) \ (2.5 \times 10^{-3}) \ 1. \text{ atm.} = 0.61 \text{ cal.} \tag{12}$$

$$w = \int_{\Delta V = 0}^{\Delta V = 2.5} P d\Delta V = \int_{\Delta V = 0}^{\Delta V = 2.5} K\Delta V^2 d\Delta V = 2.00 \text{ cal.} \tag{13}$$

$$w = \int_{\Delta V = 0}^{V\Delta = 2.5} P d\Delta V = \int_{\Delta V = 0}^{V\Delta = 2.5} K'\Delta V^3 d\Delta V = 1.54 \text{ cal.} \tag{14}$$

It is apparent from these calculations that $\Delta F_s{}^{P/a}$ and ΔF_e are at least large enough to provide energy of the right order of magnitude for the above compressions. But $\Delta F_s{}^{P/H_2O}$ is not, which is consistent with the experimental result that wet sintering alone did not effect complete compaction of the agglomerate.

As was mentioned earlier, water evaporation and film formation are concurrent events. This removes $\Delta F_s{}^{P/a}$ as a reasonable choice for energy source in the film-forming process.

There remains ΔF_e which, from its magnitude, is the most attractive choice anyway. It seems reasonable to suggest that the work contributed to the film-forming process by the capillary mechanism derives its energy from ΔF_e. Moreover, in considering other mechanisms whereby the incipient film can convert energy to work, it is necessary that such mechanisms be consistent with ΔF_e as the energy source. The diffusion theory which will now be described fulfils this requirement.

The Diffusion Theory. The essential features of this mechanism are: (*1*) water diffuses through the polymer particles in the surface of the film

and a compressive force normal to the surface is thereby generated; (*2*) the magnitude of this compressive force is limited by the tensile strength of the latex, by P_n, or by the osmotic pressure whichever is less; (*3*) the energy for this process is supplied as heat from the surroundings. This heat is converted to useful work by evaporation of the water. The maximum amount of work which can be done is ΔF_e.

The operation of the diffusion force can be explained by considering a cylindrical vessel completely filled with water and covered with a frictionless piston which is permeable to water vapor but not to liquid water. When this vessel is placed in an atmosphere of low relative humidity, the water evaporates, and the liquid exerts a negative pressure on the piston the magnitude of which cannot exceed the osmotic pressure or the tensile strength of water (40 kg./cm.²), whichever is less. The magnitude of the osmotic pressure, π, is defined by the equation

$$\pi = (RT/0.018) \ln(P_1°/P_1) = (RT/0.018) \ln (100/\text{R.H.})$$

where $P_1°/P_1$ is the ratio of the vapor pressure of pure water to the vapor pressure of water in the vapor phase and R.H. is the relative humidity (in per cent). From this it is calculated that at 25°C. a relative humidity of 97% will produce an osmotic pressure of 40 kg./cm.² Thus, under ordinary drying conditions for latex films the pressure is limited by the tensile strength of the water or by P_n, the capillary pressure, rather than by relative humidity.

The postulate that diffusion of water through the polymer contributes to the film-forming force is supported by the following facts.

(*1*) A ⁷⁰/₃₀ (VeCl₂)/(n-BA) copolymer latex dries more slowly than does an analogous ⁶⁷/₃₃ (EA)/(MMA) one. This means that with the latter more water is being transported through the polymer. This is what one would expect since the EA/MMA copolymer is more water-permeable. The diffusion of water through the polymer must be doing film-forming work.

(*2*) A ⁶⁵/₃₅ MMA/n-BA copolymer latex film when covered directly with a thin (0.7 mil.) solvent-deposited ⁹⁵/₅ MMA/n-BA film dried to a clear continuous film at room temperature. An identical latex film cast alongside the above and dried at the same rate, etc., but without the ⁹⁵/₅ MMA/n-BA film in direct contact with it, did not form a continuous film. This shows that capillarity is not necessary for film formation and that diffusion of the water through the solvent-deposited polymer film contributes to the film forming force.

(*3*) As mentioned earlier, the rate of water evaporation from a drying latex film is much greater than would be predicted were water to leave only by way of the air–water interface.

General Picture of Film Formation

The sequence of events involved in conversion of a latex to a coherent film can be described as follows. Water evaporates until the system

becomes so concentrated that the repulsive energy between the particles is overcome and flocculation occurs. At or about this point the spheres in the surface begin to emerge from the liquid and are consequently subjected to the forces of capillarity, G_n and G_p. G_n tends to push the particle normal to the surface and thereby exerts a compression on the matrix of particles under the surface. In response to this stress the interior particles individually begin to deform and/or the matrix of spheres undergoes compaction. Such deformation and compaction squeezes water to the surface so that the surface layer of particles remain at least half immersed. The force normal to the surface, G_n, of course, increases as the line of contact between polymer, air and water moves downward over the upper hemisphere of each particle in the top layer and reaches a maximum when the particles are just half immersed. Thus, the system at first tends to be self-regulating, the level of water being automatically regulated so as to produce the required normal force.

Concurrent with the compaction normal to the surface, distortion of the surface layer of particles is occurring under the influence of G_n and G_p in such a way that the surface holes are being squeezed shut.

If $\Delta F_s^{P/H_2O}$ is significant, it is reasonable to expect that wet sintering is also contributing to the forces fusing the particles during this early part of the compaction process.

During this time, while water is being evaporated from the air–water interface, water is also diffusing through the particles in the surface and being evaporated therefrom. This exerts a compacting force normal to the surface. As the compaction of the system proceeds, the area of the air–water interface will decrease. Moreover, the vapor pressure of the liquid water in the surface holes will progressively decrease with the decrease in the radius of the holes. Consequently, diffusion through the particle will play an increasingly significant role.

Due to the influence of G_n, G_p, wet sintering, and the diffusion force, the surface holes essentially disappear and the remaining water must leave by diffusion. The compressive pressure generated thereby completes the compaction process to give a polymer film with essentially no void spaces present.

Although the polymer particles are now completely compressed together, the interface between the original particles remains more or less intact. The adsorbed surfactant groups comprising this interface gradually congregate together over a period of days under the impetus of the residual surface free energy and the free energy of association of the surfactant molecules. Particle-to-particle contact thus becomes more intimate as time progresses and the film improves in tensile strength and water resistance. In most instances, however, the original particle-to-particle boundaries are never completely obliterated. This is evidenced by the tendency of films cast from large particle latexes to give more opaque films when reswollen with water than those cast from small particle size latexes.

Summarizing then, it appears that film formation takes place as the

results of several different mechanisms.   Early in the compaction process capillarity, wet sintering, and diffusion all play complementary roles, the relative magnitudes of which depend on F_s^{P/H_2O}, particle diameter, water permeability of the polymer, $\gamma_{H_2O/a}$, and contact angle between polymer and water for the particular latex involved.

At later stages—probably after compaction is roughly half complete— the diffusion process assumes a completely dominant role, and the contributions from capillarity and wet sintering become negligible.

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Résumé

Une nouvelle théorie du mécanisme de formation de film de latex est présentée. Les données essentielles de cette théorie sont que (1) la source principale d'énergie de formation du film est la chaleur environnante; cette chaleur est convertie en travail utile (filmogène) par évaporation de l'eau; le film initialement formé en est le moteur. (2) un mécanisme important, au cours duquel l'évaporation de l'eau effectue un travail utile, est la diffusion de l'eau à travers les particules de polymères elles-mêmes. Les contributions de la capillarité et de l'humidité au processus filmogène sont analysées; elles sont les plus importantes au cours de la première moitié du processus de coalescence des particules. On présente des faits expérimentaux qui appuient cette théorie.

Zusammenfassung

Eine neue Theorie zur Erreichung eines besseren Verständnisses des Mechanismus der Latexfilmbildung wird aufgestellt. Die wesentlichen Züge dieser Theorie sind: (1) Die Hauptenergiequellen für die Filmbildung ist die Wärme der Umgebung; diese Wärme wird durch Verdampfung des Wassers in nützliche (Filmbildungs-) Arbeit umgewandelt; dabei bildet der entsprechende Film die Maschine; (2) einen wichtigen Mechanismus, durch welchen die Wasserverdampfung nützliche Arbeit leistet, bildet die Diffusion des Wassers durch die Polymerteilchen selbst. Die Beiträge der Kapillarität und der feuchten Sinterung zum Filmbildungsprozess werden analysiert; sie besitzen die grösste Bedeutung während der ersten Hälfte des Teilchenkoaleszenzprozesses. Experimentelle Belege für das oben entwickelte Bild werden gegeben.