

## Formation of Films from Polymer Dispersions

GEORGE L. BROWN, *Rohm & Haas Company, Philadelphia, Pennsylvania*

### INTRODUCTION

The deposition of continuous films from polymer dispersions is a process of increasingly great industrial importance. The products of emulsion polymerization find expanding consumption directly in disperse form in uses which require, with only occasional exceptions, the ultimate formation of a continuum of polymer. In the laboratory, the preparation of films from dispersions offers a convenient technique for securing test specimens. From a theoretical standpoint, the mechanism of the formation of continuous films from dispersed spherical particles is of intrinsic interest.

Previous considerations of the mechanism of film formation from emulsions have in reality treated the sintering of solid particles which lie in juxtaposition following evaporation of the water, with air occupying the voids space. This process, although of interest, may differ in important respects from that by which films are deposited from many water-borne dispersions.

Our purpose is to present a mechanism which qualitatively accounts for the important known features of film formation from emulsion polymers, and which is solved in quantitative fashion following the adoption of simplifying assumptions.

### PREVIOUS TREATMENT OF THE PROBLEM

Two publications by workers at Dow Chemical Co. have presented the fullest previous treatment of the mechanism of film formation.<sup>1,2</sup> In the first article, they consider the fate of two particles placed in contact, which coalesce in the manner shown in Figure 1.

The progress of this fusion should follow an equation of Frenkel, expressing the half-angle of contact,  $\theta$ , as a function of the surface tension  $\sigma$ , the time  $t$ , the polymer viscosity  $\eta$ , and the particle radius  $r$ :

$$\theta^2 = 3\sigma t / 2\pi\eta r$$

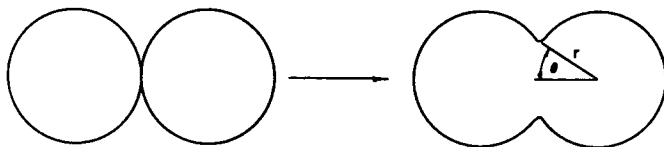


Fig. 1. Fusion of contiguous particles by viscous flow.

These authors describe **film formation** as follows: "The sintering of synthetic latex particles takes place by the viscous flow of the polymer, the surface tension of the plastic furnishing the necessary shearing stress." They observe experimentally that the angle of contact between pairs of particles is related to the radius as predicted by the equation. They further state that "as the water evaporates, the colloidal polymer particles are deposited upon the surface where they fuse into a film."

In the second article, the process of film formation is described as occurring in two steps: "loss of water to a point of irreversible contact of the particles, and a fusion or actual development of the film."

The mechanism by which particle contact is established is not discussed. Fusion is assumed to occur under the action of the surface tension of the polymer, tending to minimize surface area. The pockets formed between particles are rendered spherical by the influence of surface tension, and the spherical voids spaces shrink if the compressive strength of the polymer is sufficiently small to allow deformation into the cavity.

Although the treatment may be correct for the sintering of dry polymer particles, we suggest that it is not the mechanism of film formation in the more usual cases, because:

(1) It is observed that film formation in many polymer emulsion systems occurs concurrently with the evaporation of water, and is complete when water evaporation is complete. **In this case, the surface tension of the polymer could not supply the driving force.** Rather, this would be replaced by the polymer-water interfacial tension, which in the presence of the emulsifier would in general be lower in value than the surface tension. By analogy with oil-water systems which can be measured, it may be in the range of 0-10 dynes/cm., rather than about 30 dynes/cm., as postulated by these workers. In addition, it would be remarkable indeed if the times required for water evaporation and particle coalescence were so comparable for a wide variety of polymers unless the processes were interdependent.

(2) It may be demonstrated experimentally that the rate of water removal may determine the coalescence of polymers of borderline "film-ability." This rate may be altered by changes in substrate capillarity or in the relative humidity of the surrounding atmosphere.

(3) Porous, incompletely coalesced films may be formed from many polymers simply by maintaining, during water evaporation, a temperature lower than a certain critical value. It is observed that for certain polymers a higher temperature exists which is insufficient for coalescence of the porous structure previously formed at a lower temperature, but is adequate for complete coalescence if applied during the entire course of water evaporation. In addition to the plasticization of polymers by the water, the water exerts a strong force responsible for coalescence. The role of water in the process is of extreme importance.

(4) Lightly crosslinked emulsion polymers may form films which are continuous, though lacking in strength. Purely viscous flow is not possible in such a system, and presumably the particles have deformed and the

surface cohered, but interpenetration by self-diffusion has not occurred. Thus, film formation is possible in the absence of purely viscous flow.

Certain of these limitations have been recognized by Wheeler, Jaffe, and Wellman,<sup>3</sup> who have not, however, suggested a suitable over-all mechanism.

## A PROPOSED MECHANISM FOR FILM FORMATION

### (A) Energetics

From the standpoint of energetics, the process of coalescence of polymer droplets into a film is favorable because of the decrease in free energy achievable with minimization of total surface, where:

$$\Delta F = \sigma \Delta A$$

where  $\Delta F$  = free energy change,  $\sigma$  = surface or interfacial tension of polymer, and  $\Delta A$  = change in surface area of polymer.

Eventually all contiguous particles would flow into a deformed sphere representing a minimization of surface and gravitational energy. From a practical standpoint, for many systems this "never" happens, whereas, in others, coalescence of small particles into a film occurs almost instantaneously.

Although the energy change may be favorable, important limitations may exist which prevent accomplishment of the process. For example, a high activation energy may make the process improbable. Although two contiguous spheres will fuse in a time dependent manner, they must first be brought into contact. The process is improbable if this is not done, and a suitable mechanism must exist to accomplish it. In addition, the driving force may be of sufficient magnitude, but insufficient as to time of duration, such that the process is not completed. It is appropriate, therefore, to examine the process step by step.

### (B) A History of Film Formation

Our model system initially consists of a dispersion in water of spheres, generally 0.1 to 1.0  $\mu$  in diameter, which comprise up to about 60% by volume of the total system. As water evaporates from the surface, the particle centers approach each other, but the particles remain separate (*i.e.*, they are deflocculated), until they are forced into contact by spatial limitations.

For optimum ease of coalescence, deflocculation is necessary, and the particles will pack efficiently upon loss of water. Where flocculation occurs, a spongy structure may result which hinders final coalescence. That is, the particles may be strongly coherent in the form of loose networks or aggregates. The forces available for coalescence will be smaller and the forces needed may be larger than where efficient packing is possible, as will be discussed below.

A comparison with the behavior of pure clays which disperse readily in water with well-structured soils may be instructive. During drying or sedimentation, the dispersed clay particles pack efficiently into a dense cake. A soil of good tilth is not so dense because it does not shrink, and leaves larger voids spaces which are desirable for water holding and aeration. In the final stages of drying, the clay exhibits "mud cracking" to relieve the stress of shrinkage, whereas the structured soil does not. In contrast, soft polymers do not show such "mud cracking" because their deformability allows dissipation of the stress. Harder polymers may form continuous, but segmented films, because stress dissipation is insufficient, whereas still harder polymers are nonfilm forming.

This initial increase in the concentration of the dispersion occurs during the first stage of film formation, during which water is evaporating from an unbroken surface film. The second stage begins when the particles can no longer slide over each other into new positions. Beyond this point, both water and polymer appear on the surface, and either of the following occurs: (1) The particles do not deform, and water evaporates, eventually vacating the channels which pervade the polymer network. (2) The particles deform and film formation proceeds.

The fact that the particles of the dispersion may or may not be deformed into a homogeneous film implies that there are certain forces acting to achieve coalescence and other forces acting to resist it, and that the condition for film formation could be expressed as an inequality between these forces. Let us examine what these may be.

At least four forces are exerted which tend to coalesce the polymer particles:

$F_s$  = force produced by negative curvature of polymer surface. This occurs *only after two (or more) particles come into contact*. The internal pressure in a sphere of polymer is given by:

$$P = 2\sigma/R$$

where  $\sigma$  = surface (or interfacial) tension and  $R$  = radius. But this pressure cannot act in any manner except to maintain sphericity if the particle is not touching another. When two particles are in contact, however, the resultant forces are as shown in Figure 2, and these forces tend toward production of one large sphere. In a liquid-like structure, stability will re-

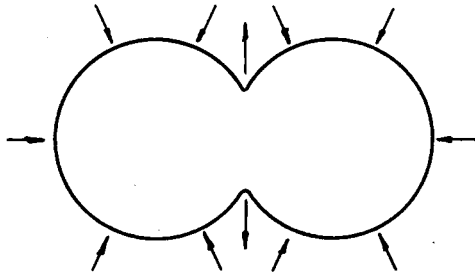


Fig. 2. Forces on fusing particles resulting from surface curvature.

sult only if hydrostatic pressure is equal throughout, which requires equal curvature at all points on the surface.

$F_C$  = capillary pressure resulting from the presence of a water surface of negative curvature in the interstitial capillary system which is present during the period of water loss. This force is not present in the original dispersion and begins to operate only after the solids are increased to a certain critical level.

$F_v$  = the van der Waals attractions between the spheres which are the normal attractive forces leading to flocculation or coalescence of emulsions and dispersions.

$F_g$  = the gravitational force which leads to settling in a dispersion and compaction in a deformable powder.

The forces resisting coalescence of the particles are:

$F_G$  = the resistance of the sphere to deformation.

$F_e$  = the coulombic repulsion of the charged spheres.

Film coalescence will proceed if the polymer particles compact, constantly increasing the volume fraction of polymer, until the ultimate limit of a homogeneous continuum of polymer is reached.

If coalescence is occurring at any instant, the following inequality must exist:

$$F_v + F_C + F_v + F_g > F_G + F_e$$

This inequality must be maintained for every step in the process if complete coalescence is to be achieved.

The influence of the polymer-water interfacial tension deserves attention. The pressure resulting from the existence of the interfacial tension can aid coalescence only when a concave polymer surface is presented to the water. Initially a convex surface exists, and if the interfacial tension is ever to serve as a driving force a mechanism for bringing it into effect must exist. In addition, if the interfacial tension is low, as is probable with surfactant present, the influence of this force becomes small when compared with the capillary pressure. Since this force is nonexistent or small during early stages, as compared to capillary forces, it will be neglected. If the force becomes appreciable, our final conditions for film formation will be more conservative as a result.

In view of the excellent stability of many of the emulsions on long-term standing, it is assumed that the coulombic repulsion is greater than van der Waals' attraction at distances comparable to the radius of the particle (the spacing of particles in a relatively concentrated dispersion). The gravitational force is quite negligible.

On the other hand, the magnitude of the capillary forces can be quite large, as will be demonstrated.

The importance of capillarity in compressing inorganic and organic colloids was recognized by Kistler, and is the basis for his patents and articles<sup>4</sup> on the production of aerogels, which are foamed structures produced by the avoidance of the normal capillary compression which tends to compact aqueous gels upon drying. He finds it possible to remove a pene-

trating liquid at its critical temperature, where the surface tension becomes zero.

In order to handle this problem we shall simply drop consideration of all of the forces except those due to capillarity and resistance to deformation. In principle, certain estimates could be made and a more exact solution sought. For the present, we shall describe the conditions for film formation by the inequality:

$$F_c > F_g$$

which must be true for duration of the entire process.

Considering the problem in this manner, we must be concerned with the course of events after the spheres have been concentrated as much as is possible without deformation. Our system now consists of two interpenetrating continua—spheres in contact and water pervading the voids space. Only one phase is continuous on the surface—the assemblage of touching convex polymer areas, which contain isolated concave areas of water. The capillary pressure arises as a result of the presence of the latter, and this provides the major driving force for film formation.

This capillarity may be considered to act in the same manner as an overall compression on the particle assemblage. In actuality, it is exerted in a direction normal to the water-particle interface and tends to deform the particle in this direction, as shown in Figure 3.

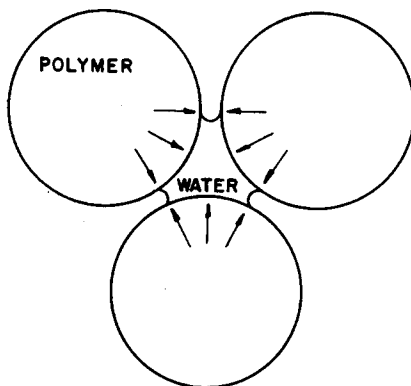


Fig. 3. Contracting forces resulting from capillary water in particle interstices.

With a polymer of sufficient rigidity to resist deformation during the duration of the capillary pressure, water will evaporate without particle coalescence. As evaporation proceeds, water disappears from the successive interior layers of the particles, and once the water has disappeared from the recess adjoining a particle the force tending to move that particle normal to its surface disappears. Thus, if the capillary force is insufficient, the progression necessary for coalescence is broken.

On the other hand, if the capillary force is greater than that required, no harm is done because of the presence of a self-regulating effect. Should

the polymer deform too quickly, water would be squeezed to the surface, the radius of curvature of the water surface would be increased, and the driving force causing the deformation would be decreased. Thus a balance is maintained.

If the stress remains sufficient to produce the required deformation, film formation should proceed. The force for deformation now changes in two respects. The area of contact between spheres increases, and if the deformation is completely elastic the required thrust increases monotonically. However, if viscous flow is possible, the particle undergoes stress relaxation, and the exact course of the required stress is a function of the complex modulus of the polymer, the geometry of deformation, and the time. Simultaneously, the capillary force is altered. So long as interconnecting cells exist, and the curvature of the water surface increases as the voids space shrink, the capillary pressure increases. However, it is exerted over a smaller area, since the area of contact between water and polymer decreases. Thus, the resultant total force for compression may increase initially, but eventually approaches zero as the last film of water disappears.

In the light of these conditions, we may describe the course of events accompanying water evaporation from polymer dispersions for two extreme cases—those of purely elastic deformation and purely viscous deformation. Actual polymers should behave in an intermediate manner.

With a dispersion of polymer purely elastic in deformation, the stress will increase with progressive achievement of coalescence, depending solely upon the configuration of the particles. The stress will be time-dependent only to the extent that the water evaporation, and therefore the configuration, are time-dependent processes.

At some point in the process, the capillary force will be insufficient and deformation will cease. As the water evaporates, wetting of the particles is lost, and the capillary force is lost. If the adjacent particles are sufficiently attracted or bonded, the partial coalescence is maintained. If not, the spheres should rebound to their original shape.

If pure viscous Newtonian flow exists, the polymer will always deform proportionately to the applied stress. The required stress does not build up as a result of the increasing area of contact of spheres. Providing the flow is sufficiently rapid to move polymer into the voids space as the water is withdrawn by surface evaporation, coalescence occurs as the water evaporates. The particles will eventually coalesce, even in the absence of water, as the result of gravitation and the surface tension of the particles, although this might be much slower than with water present.

### (C) Quantitative Solution

An exact solution to the problem would involve an examination of the differential process of film formation. That is, at each point in the process we would require a knowledge of the capillary forces in existence and the rate of change of the configuration under these forces. If the differential

equation could be written expressing it as a function of the constants of the system and the change of water content, integration between suitable limits would give a value for the total time required. Although this problem may be soluble in principle, it would require an intimate knowledge of a number of factors which would be difficult to obtain. A first approximation of the solution has therefore been made as follows.

The resistance of the spheres to deformation is calculated on the basis of a model which consists of two spheres pressed together until their centers are separated by the distance of separation of centers that would exist in close-packed dodecahedra of identical individual volumes. The average pressure over the area of contact is calculated. The total force required is expressed in terms of a geometric factor and  $G_s$ , the shear modulus of the film measured by observing the strain resulting from application of stress for a duration of time,  $t$ , equivalent to that available for film formation.

The force available for film formation is considered to be that available initially in a system of close-packed uniform spheres. This force operates over the entire area of contact between water and polymer, in a direction normal to the interface. No correction is attempted to calculate resultant forces of capillarity and of resistance to deformation so that they are operating in parallel directions, but this correction is probably small.

#### (1) Calculation of Capillary Pressure

As the water evaporates from the close-packed spheres the capillary pressure increases, and reaches a maximum if the water level reaches that of the "throat" of the interstitial capillary. The "throat" is the narrow capillary which exists in the plane passing through the centers of three contiguous particles.

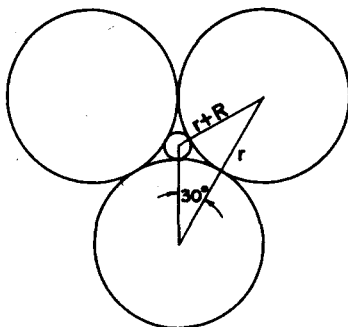


Fig. 4. Approximation of pore size for calculation of capillary pressure.

Considering an array of three close-packed spheres of radius  $r$ , as shown in Figure 4, we find:

$$r/(r + R) = \cos 30^\circ$$

$$R = 0.155r$$

and:

Therefore: 
$$P_C = \sigma \left( \frac{1}{R} + \frac{1}{R} \right) = 12.9 \frac{\sigma}{r}$$



Since the volume fraction occupied by close-packed spheres is 0.740, the centers will be separated on the average by  $0.740^{1/3} (2R)$  following complete elimination of voids. Considering the deformation of two spheres pressed together to this distance of separation, we arrive at an estimate of the force resulting from the resistance of spheres to deformation. This may be done by a standard method, as found in Prescott,<sup>5</sup>

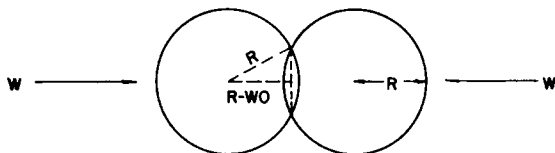


Fig. 5. Deformation of two spheres pressed together.

If the pressure at a point at a distance  $r$  from the center of a circle of contact of radius  $a$  (as shown in Fig. 5) is:

$$p = C(a^2 - r^2)^{1/2}$$

where  $C$  is a constant, then the deflection at the same point is:

$$w = w_0[1 - (1/2)(r^2/a^2)]$$

$$w_0 = (1 - \nu)\pi Ca^2/4G$$

where  $G$  and  $\nu$  are shear modulus and Poisson's ratio, respectively. The total thrust on the circle is, by integration:

$$W = \int p dA = (2\pi/3)Ca^3$$

As a first approximation, it should suffice to take:

$$w_0 = R - (R^2 - a^2)^{1/2}$$

Also, for elastomers,  $\nu = 0.5$ , hence the total force is:

$$\begin{aligned} W &= w_0 \frac{(2\pi/3)Ca^3}{[(1 - \nu)\pi Ca^2/4G]} = \frac{16G}{3} aw_0 = \frac{16G}{3} a[R - (R^2 - a^2)^{1/2}] \\ &\cong \frac{16G}{3} w_0(2w_0R)^{1/2} \quad (\text{since } w_0 \ll R) \end{aligned}$$

Thus the average pressure on the circle of contact is:

$$\bar{P} = \frac{W}{\pi a^2} = \left[ \frac{16G}{3\pi} \right] \left[ \frac{R - (R^2 - a^2)^{1/2}}{a} \right] = \left[ \frac{8(2)^{1/2}}{3\pi} \right] G \left[ \frac{w_0}{R} \right]^{1/2}$$

Haines<sup>6</sup> tested the capillary pressure of water passing through an array of close packed uniform spheres small enough to exhibit appreciable capillary pressures but large enough to permit careful packing. He obtained a maximum pressure of  $11.3\sigma/r$  as compared with  $12.9\sigma/r$  predicted by theory.

The magnitudes of the pressures involved are given in Table I, for a series of particle sizes, and for surface tension values of 30 and 70, which are about the extreme values which would be found for aqueous systems.

TABLE I

PRESSURE *vs.* PARTICLE SIZE FOR  $\sigma = 30$  AND  $\sigma = 70$ 

Particle diam., microns	Pressure, kg./cm. <sup>2</sup>	
	$\sigma = 30$	$\sigma = 70$
1.0	7.9	$1.8 \times 10^1$
0.1	$7.9 \times 10^1$ (= 80 atm.)	$1.8 \times 10^2$
0.01	$7.9 \times 10^2$ (= 800 atm.)	$1.8 \times 10^3$
0.001	$7.9 \times 10^3$	$1.8 \times 10^4$
0.0001	$7.9 \times 10^4$	$1.8 \times 10^5$

(2) *Resistance to Deformation*

Compression of an array of hexagonally close-packed spheres would result in the deformation of the spheres into rhombic dodecahedra. We shall consider that the total polymer volume remains constant (*i.e.*, the Poisson ratio is 0.5).

The force required to deform the particles to a predetermined extent will be a product of the modulus of the polymer and a geometric constant, providing uniform, close-packed spheres are being compressed, and will be independent of the size of the spheres:

$$F_G = kG_t = f(t, T, \text{polymer})$$

From geometric considerations:

$$R - w_0 = 0.905R$$

and:  $w_0 = 0.095R$

Therefore:  $P = 0.37G_t$

where  $G_t$  is the shear modulus measured by examining the strain resulting from the application of a stress for the length of time,  $t$ .

(3) *Conditions for Film Formation*

In previous sections, we have proposed as the condition for film formation:

$$F_C > F_G$$

and have derived, on the basis of the stated approximations, values for each:

$$F_C = 12.9 (\sigma/r)A$$

$$F_G = 0.37G_tA$$

From these we obtain, as our condition for film formation:

$$G_t < 35\sigma/r$$

Again assuming surface tension values of 30 and 70 dynes/cm.<sup>2</sup>, we obtain the maximum value of the polymer modulus which will allow coalescence for particles of various radii (Table II).

TABLE II

Particle radius, $\mu$	Maximum modulus, $G_t$ , for film formation	
	$\sigma = 30$	$\sigma = 70$
1.0	$1.1 \times 10^1$ kg./cm. <sup>2</sup>	$2.5 \times 10^1$ kg./cm. <sup>2</sup>
0.1	$1.1 \times 10^2$	$2.5 \times 10^2$
0.01	$1.1 \times 10^3$	$2.5 \times 10^3$

An exact specification is necessary for the method for experimental determination of the modulus. The water-saturated polymer should be subjected to small stresses and the strain determined as a function of time. The time required for evaporation of water after the particles have reached close packing is observed, and the modulus value corresponding to this time is obtained.

The minimum temperature for film formation is that at which the modulus,  $G_t$ , is less than the maximum value specified in Table II. A modulus-temperature curve typical of a number of acrylate-methacrylate copolymers is shown in Figure 6, where the modulus has been computed on the

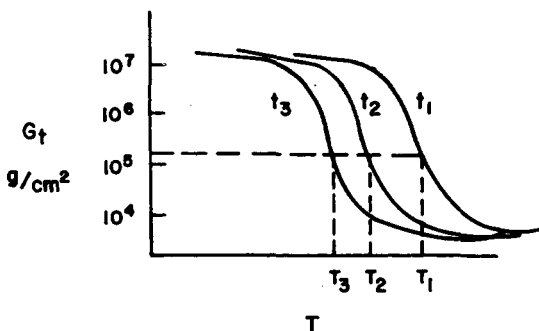


Fig. 6. Modulus-time-temperature relationships showing conditions for film formation.

basis of strains produced  $t_1$ ,  $t_2$ , and  $t_3$  seconds after application of stress. An emulsion of particle size  $0.1 \mu$  and 30 dynes/cm. surface tension should produce a film at a temperature  $T_1$ , or above if time  $t_1$  is the time of water evaporation (*i.e.*, duration of capillary force). Temperatures  $T_2$  and  $T_3$  correspond to longer times  $t_2$  and  $t_3$ .

## CONCLUSION

The mechanism for film formation presented accounts qualitatively for the coalescence of polymer particles in terms of the particle size and surface tension of the emulsion, the rheological properties of the polymer, the temperature, and the rate of water evaporation. An approximate quantitative solution is presented.

Results of film formation in actual emulsion polymers are qualitatively in accord with predictions, and film formation occurs at temperatures close to those predicted by the theory. The sharp change in modulus with temperature in the transition region, however, would lead to only small differences in the predicted temperature even if a rather large alteration was made in the critical modulus value specified.

Exact experimental comparisons will require a more intimate knowledge of the rheology of the water-saturated polymer, a specification of the temperature of the drying emulsion, and a determination of the drying time, for emulsions of uniform spheres. Improvements in the theoretical treatment would require a better specification of the model system than is now possible.

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### Synopsis

Polymer emulsions will undergo film formation upon loss of water if the driving force provided by capillary pressure is sufficient to overcome the resistance of the polymer particles to deformation. The conditions for film formation are expressible in terms of the surface tension and particle size of the dispersion, the time available for the drying process, the temperature, and the rheological properties of the polymer.

### Résumé

Les émulsions de polymère peuvent donner lieu à la formation de film par perte d'eau, si la force exercée par pression capillaire dépasse la résistance des particules polymériques à se déformer. Les conditions de formation de film peuvent être exprimées aux dépens de la tension superficielle et de la grandeur des particules de la dispersion, au départ du temps disponible pour le séchage, de la température et des propriétés rhéologiques du polymère.

### Zusammenfassung

Bei Wasserverlust tritt in Polymer-Emulsionen Filmbildung auf, wenn die treibende Kraft, die durch Kapillardruck geliefert wird, gross genug ist, um den Widerstand der Polymerteilchen gegen Deformation zu überwinden. Die Bedingungen für Filmbildung können mittels der Oberflächenspannung und Teilchengrösse der Dispersion, der für den Trocknungsvorgang verfügbaren Zeit, der Temperatur und der rheologischen Eigenschaften des Polymers ausgedrückt werden.

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