Effect of Melamine on the Foam Kinetics of Polyurethane Model System. II. Effect of Melamine Particles on Film Formation

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ABSTRACT: To study the influence of the flame-retardant melamine on foam properties of a polyurethane model system, single, vertical liquid foam films were studied. The presence of particles gives the possibility to observe the complete circulation in the film. The films of the model system have been found to be mobile films showing marginal regeneration. Film formation was combined with surface-tension measurements on the pool surface. The changes in the surface tension of the pool were measured and the amount of surfactant diffused from the surface of the pool to the surface of the film were calculated. This quantity was found to be a few percent of the moles necessary for equilibrium coverage. The fresh film surface is nearly independent of the pool surface and the meniscus behaves as a slit, producing a film with a nearly surfactant-free surface. Two characteristic phenomena were observed during film formation from a suspension containing 25 pphp melamine ultrafine: (1) The convective currents are slower in the melamine-filled film than in the corresponding melamine-free lamellae. (2) No surface tension difference was seen on the surface of the pool after film formation. It seems that the melamine hinders the surface diffusion. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci **67:** 1739–1752, 1998

Key words: film formation; high viscous system; polyurethane model system; melamine; marginal regeneration

INTRODUCTION

Flexible polyurethane foams are used in seating and bedding; therefore, the addition of flame retardants is necessary. Melamine, in the form of solid particles, fulfills this purpose. However, it is well known from the literature that solids influence the stability of foams. In our work, the effect of melamine particles on film formation was studied in a polyurethane model system (polyol, surfactant, melamine).

The stability of foams can be investigated by single foam films, which represent correctly many of the foam characteristics. Mainly, the rate of thinning and the lifetime of foam films were measured and correlated with other solution properties such as static and dynamic surface tension, viscosity, and the width of the film.[1–3]

The thinning of films has always interested researchers since the stability of foam films mainly determines the stability of the foam. The liquid films thin as a result of capillary and gravitational forces. Thinning takes place by a laminar flow

and/or turbulent motion. To better understand this article, this flow will shortly be described as an introduction.

Laminar Flow

Menisci existing along the vertical legs of the frame and as well as the meniscus at the bottom of the film are curved in such a way (concave outward) that the pressure in the menisci is smaller than in the film. This pressure difference results in liquid flow from the lamella to the menisci between the surfaces of the film. The surface tension gradient developed in the surface layer slows the flow down, but the mechanism of the thinning is not influenced.

Turbulent Flow

The other possible mechanism of thinning is the movement of film parts and their surfaces as units. In vertical mobile films, turbulent motions can be seen along the vertical borders and at the lower horizontal meniscus. The drainage rate is found to be dependent on the width of the frame.[1,2] From the experimental results, it could be concluded that there must be a different thinning mechanism for vertical mobile films than for other types of films. The explanation is the so-called marginal regeneration which is the precursor of the above-mentioned turbulent flow. Marginal regeneration is not seen in horizontal films. The observation of marginal regeneration has already been published by Gibbs[3] and it was explained by Mysels et al.[1] as the dominating mechanism for film drainage.

According to Mysels et al., the capillary force acting on thicker film parts is larger than the force acting on the thinner parts. The difference of the forces creates a flow in which the thicker film parts, together with their surfaces, are sucked into the border (outflow), while the thinner ones are drawn out (inflow). This process is known in the literature as marginal regeneration. The Marangoni effect also influences the rate of this flow, but the mechanism is not affected.

The above-mentioned two types of thinning differ in the surface area taken by the flow. In large vertical films, the thinned film elements rise from the film/meniscus transition. Their motion differs if they are created at the horizontal or at the vertical meniscus.

 1. At the bottom of the film, thinner film parts

are developed with a given repeat distance. Baets[4] studied the wavelength of the rising film spots in marginal regeneration and it was compared with nonhomogeneities of horizontal films. Baets found a linear relationship between the thinning velocity and the bulk viscosity of the foaming liquid. Surface waves are generated in the meniscus and they spread over the film. The peacock feathers (thin parts) rise up to that film part having a thickness that equals their own thickness.

 2. At the vertical borders, the thinner film parts meet each other during rising, resulting in a turbulent motion.[1] These spots generally join each other under the upper horizontal bar of the frame.

In the literature, the rising spots are mentioned, but their origin and their motion are not entirely discussed. In vertical films, their rise is explained by a lifting power without further explanation. Recently, Stein[5] reported on the direction dependence of marginal regeneration which is explained by the surface tension gradient vertically in the film.

An increase in the bulk and/or surface viscosity will retard the flow of liquid in the film and help to stabilize the foam. A relationship between the surface viscosity and foam stability was found experimentally by Kendrick et al. in a polyurethane model system.[6] Frankel et al.[1] considered the thickness of film drawn out of a border and that of film which falls into the border as a function of drawing rate (Frankel's law). Frankel's law is a good prediction for films formed from sodium dodecyl sulfate solutions.

Recently, the formation of film from sodium dodecyl sulfate-containing polymers was studied.[7,8] It was concluded that Frankel's law is not applicable for viscous solutions containing polymers; the description of the surface layer is given in the case of both soluble and insoluble surfactants.[7]

Prins and van Voorst Vader[9] found a limit in surface elasticity when marginal regeneration may take place. The direct observation of films can give useful information about the processes occurring in the film. Hudales and Stein[10] observed upward and downward flows in the Plateau border (by tracers) and the upward flow was explained by them as a Marangoni flow. According to them, the Marangoni flow is the result of the exchange of film elements with high surface tension and the liquid of Plateau borders which has a lower surface tension. The thickness of Plateau

borders was measured by them at different heights.

To determine the surfactant balance, the surface tension was measured on expanding surfaces[11,12] after the pioneer work of Mysels et al.[13] Most of the mentioned investigations have been done in aqueous systems.

In the initial period of polyurethane production, the rising foam must be stabilized while the bubbles are growing and the foam films are dilated. The foaming properties and the surface properties of a polyurethane model system containing melamine was studied before.[14] In this article, the film-formation properties of high viscous polyol dispersions with and without melamine particles are studied. In aqueous films, a convenient method to study thinning and the movement of the thinner film elements is the light interference measurement. In viscous polyol lamella, the drainage is slow and the film is very thick. The lifetime of a film formed from the conventional system (0.8 pphp Tegostab BF 2370/ Voranol CP 3322), in a frame of 2 × 2 cm at 298 K, is more than 8 h. Therefore, interference experiments were not performed. In single films of a polyurethane model system, the motions can be followed by tracer particles. Our conclusions were drawn from visual observations and surface tension measurements.

EXPERIMENTAL

Materials

The following materials were used: *Voranol CP 3322* (polyether polyol, DOW): viscosity (298 K), 510 mPa s; surface tension, 32.8 mN/m; hydroxyl number, 47.5 mg KOH/g; molecular weight, 3400 g/mol; water content, 0.027%; density, 1.0196 g/ cm^3. *Tegostab BF 2370* [*organo-modified poly- (ether siloxane) surfactant, Th. Goldschmidt*]: density (298 K), 1.035 g/cm^3; viscosity (298 K), 850 mPa s; solubility, soluble in polyols and in water. Average molecular weight, 10,000–12,000 g/mol (given by Goldschmidt). Tegostab BF 2370/ Voranol CP 3322 solutions will be called a conventional system in this article. *Melamine* (2,4,6-tri- amino-1,3,5-triazine; DSM Melamine). The water content is max 0.1% and that of ash and iron respectively max 0.01% and max 1 mg/kg.

The typical particle-size volume distribution measured by a Malvern Master Particle Sizer M6.10 is given below. The melamine particles were dispersed in an aqueous solution saturated with melamine at room temperature. First, the surfactant and the polyol were mixed, and, finally, the melamine was added. The components were mixed at 2500 rounds/min rotation speed for at least 30 s. The solutions were completely deaerated under a vacuum to remove the air bubbles that resulted from the stirring.

Melamine Grade	d_{50} (μm) Vol % <	d_{90} (μm) % <	d_{10} (μm) % <
45–50	58.6	81.0	43.7
Ultrafine	10.2	17.4	4.9

Methods

Both the melamine-free and melamine-filled polyol/surfactant solutions formed very stable films and foams. It was practically impossible to find the melamine effects by lifetime and foam- stability experiments. Moreover, the freshly formed films are thick[14] and do not give an interference pattern for up to 30 min. The lifetime is longer than 8 h in a frame of 2 × 2 cm size. To obtain information about the effect of melamine on the film behavior, the movement of tracer particles was followed in the film and the change of surface tension was measured during the vertical film formation.

Investigation of Film Formation by Melamine as a Tracer

Films were investigated in metal frames (Kanthal of 0.40 mm diameter) of different sizes (the width was 2 cm and the length was varied: 1, 2, or 3 cm) at different surfactant concentrations with a different melamine load. The effect of the drawing rate was studied as well. The frame was pulled out and immersed in the solution by moving the pen holder of a potentiometric recorder regulated by a function generator. All the experiments were carried out at ambient temperature. The flow rates were determined from one film only.

During film formation and thinning, the tracer particles likely follow the movement of the film element according to their diameter.[4] Bigger particles may be pushed out from the thinner film parts to the thicker film elements and smaller particles flow together with the film element. Melamine ultrafine particles in low concentration (0.5 pphp) were used as tracer particles to detect the

flows of film drawing. It was assumed that ultrafine melamine particles in a low concentration (0.5 pphp) do not change the film-formation properties of the solution and flows together with the film elements during drawing and in stationary periods. The properties of film formation were compared with films containing 25 pphp melamine ultrafine. Films were recorded by a video camera (Panasonic AG-6720A, time-lapse). The movement of particles was followed and their distance (y) from the level of the pool was plotted against the height (h) of the frame from the pool level at a given time. Both distances were divided by the total frame height (H), resulting in dimensionless axes, y/H and h/H. The character of the curves gives information about the mechanism of film formation.

Thick films containing 25 pphp melamine ultrafine particles are opaque, but during thinning, melamine-free spots arise. The movement of melamine-free film elements was followed and plotted in the same way as mentioned above.

Investigation of Film Formation by Surface Tension Measurements

The Wilhelmy plate technique (Krüss K 12) was used to measure the surface tension as a function of time while the surface area was increased by drawing a vertical film in a rectangular, closed frame in the same way as mentioned above. It is known from dynamic surface tension measurements[15] that the rate of adsorption–desorption is so small at a lower surfactant concentration (e.g., 0.08 g/100 g) that the amount of surfactant in the surface layer stays constant in the time range of the film formation.

Experiments were carried out at two different surfactant concentrations (0.08 and 0.8 pphp) with 0.5 or 25 pphp melamine present in the system at ambient temperature. Each value is the average of three to five experiments; the maximum deviation was ±0.1 mN/m.

Relation Between Surface Tension Change and Relative Surface Area Change

The relation between the surface tension change and relative surface area change was determined by the following experiments in the case of a 0.08 pphp surfactant concentration: The conventional system was poured into the measuring cell and a quasi-equilibrium situation was reached (surface tension is close to the equilibrium surface tension). The liquid level was decreased by sucking
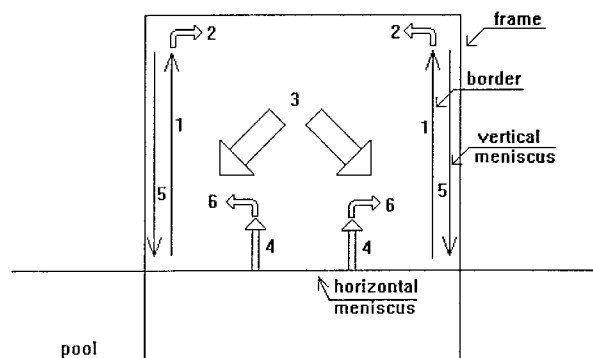
Figure 1 Schematic representation of the flows in the film.

liquid from the bottom. In this way, liquid film is created on the wall and the surface area is increased. The surface tension increase due to the surface area change was determined by the Wilhelmy plate method. The adsorption–desorption process is very slow in this system; therefore, the surface excess can be taken as constant in the time range of the experiment. The experiments were performed at ambient temperature.

RESULTS AND DISCUSSION

Stationary Film

First, we would like to describe the general processes occurring in a stationary film formed from the conventional system at a 0.08 pphp surfactant concentration in frame of 2×2 cm with a drawing rate of 0.03 cm/s. Figure 1 represents the flows in the film. Melamine ultrafine particles were used as tracers in these experiments in a 0.5 pphp load. The advantage of the tracing method is that the complete circulation of the flows can be followed.

A vertical upward flow (see Fig. 1, 0.07 cm/s, largest rate) was observed near the film/vertical meniscus transition (1) and a downward flow was seen on the legs (5). The latter process was not studied by us. This flow transports the liquid sucked from the film into the meniscus.

By following the melamine particles located far from the borders, we saw that the particles' motion has a vertical (downward, the largest rate was 0.015 cm/s) and also a horizontal component (0.01 cm/s) oriented mainly to the direction of the borders. This means that the sheet expands toward the legs of the frame on the sides (3). There is a strong horizontal streaming (0.03 cm/s) under the upper bar of the frame (2) from the

Table I Vertical Flow Rates Upward Along the Border in Stationary Films (10 s of age) at Different Surfactant and Melamine Concentrations ($v = 0.03$ cm/s, 2×2 cm Frame)

Surfactant Concentration	Flow Rate with 0.5 pphp Melamine (cm/s)	Flow Rate with 25 pphp Melamine (cm/s)
0.08 pphp	0.07	0.011
0.8 pphp	0.04	0.003

corner to the middle. It seems that the upward flow (1) slows down and turns to the middle (2). So, the film elements rise and occupy the upper area of the film. Meanwhile, the existing thicker part is pushed downward. The film part moving down expands horizontally, occupying the area of the film elements transported up.

Additionally, at the bottom of the film, film parts move upward, resulting in a turbulent motion (4). In the interference pattern, it is visible that these film parts (spots) are thinner than the neighboring parts. The thinner film parts appear with a given repeat distance. The distance of the parts can be interpreted as the wavelength.[4] In the polyol/surfactant system, the wavelength of the spots is large. At the same time, only two or three streams (0.004–0.006 cm/s, vertical) can be seen. Their motion slows down with height and they change direction (6) at a certain height. We can say that the surface transport at the vertical border is the determining factor, since the flow rate of the motions at the bottom is the smallest.

The above-mentioned rates were measured in a film with 10 s of age. The motions slow down in time; the velocity of the vertical flow in the meniscus drops from 0.07 to 0.025 cm/s after 3 min. The velocities in a film formed from the solution at a 0.8 pphp surfactant concentration is approximately half (Table I) of the rates at 0.08 pphp and it slows down in 30 s to an unmeasurable rate.

The results show that the film is mobile[1] and the horizontal components of the motions can be followed by the tracing method. In this way, we obtain information about the whole circulation of flows. The time dependence of the rate of marginal regeneration indicates that the rate is determined by the film thickness. Marginal regeneration decreases the film thickness and its velocity parallel with that.

The flows studied in stationary films are slowed down with a high melamine load (Table I, 25 pphp). The decreased rate of marginal regeneration might be caused by the increased viscosity.

Since neither the forces acting on the thin film parts nor the shear rate are known, the effective viscosity cannot be given.

Displacements During Film Drawing

The process of film drawing was expected to play a predetermining role in the stability of the film. By using the melamine particles as tracers, the film-formation mechanism can be investigated. There are two important observations:

1. The convective motions (1), discussed above in a stationary film, take place during film drawing as well. The rate of convective flows is determined. The complicated turbulent motion will be represented here by the rate of the upward vertical flow in the menisci. This flow rate is larger than the drawing rate.
2. The rate of effective film formation from the lower meniscus is a function of frame lifting. The results are shown in Figures 2–6. In the figures, the relative vertical displacement of certain tracer particles [y/H, y: particle's position from the pool level, H: total height of the frame; see Fig. 2(b)] is plotted against the relative displacement of the frame (h/H, h: position of the top of the frame from the pool level) and the slope of the obtained curves is investigated.

Depending on the movement of the particles, several cases can be distinguished. The important cases are

(a) The curves run parallel (Fig. 4): The film behaves as an inextensible lamella; there is no vertical dilatation.

From the slope of the lower, parallel traces, dy/dh, we can calculate the rate of film formation from the horizontal meniscus ($v_l = dy/dt$):
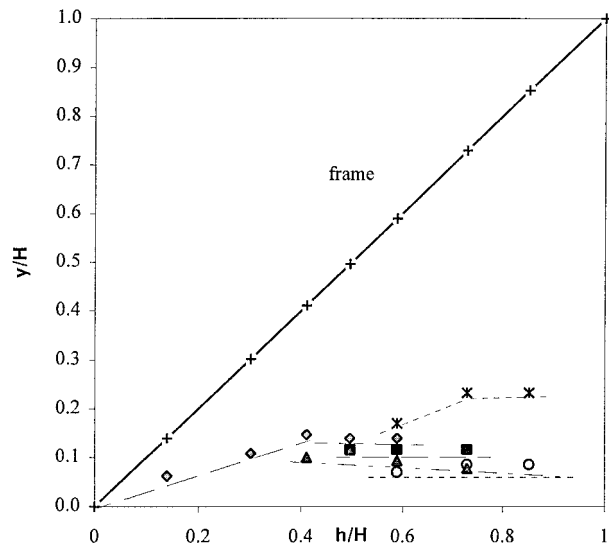
$$v_l = v \frac{dy}{dh} \tag{1}$$

(a)

(b)
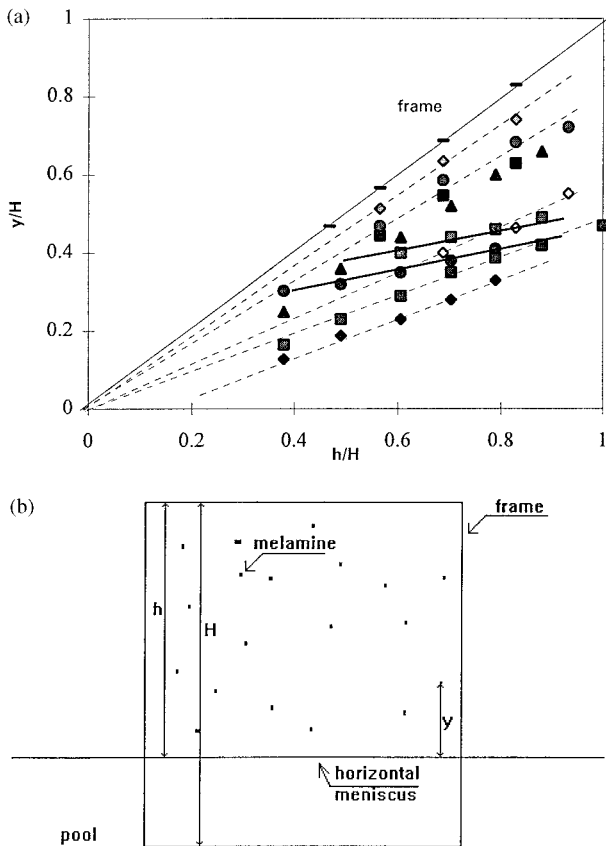
Figure 2 (a) Vertical displacements in the film formed from the 0.08 pphp conventional system + 0.5 pphp melamine ultrafine during frame lifting in frame of 2 × 2 cm with a 0.03 cm/s drawing rate. (b) Schematic drawing of melamine displacements. y, position of the melamine particle compared to the pool level; h, position of the top of the frame compared to the pool level; H, total height of the frame.

where $v = dh/dt$ is the drawing rate. If the position of the tracer particle is compared to the frame the difference $(v - v_1)$ gives the rate of film formation under the horizontal bar of the frame (v_r) only in the lack of vertical dilatation. The described rate, v_r, must be the consequence of marginal regeneration (see below), which operates during film formation.

(b) The curves run into zero and the slopes increase. The particle follows the lifting of the frame faster if it is located higher in the film (see Figs. 2 and 6). The sheet dilates vertically.

(c) The slope is different at different parts of one curve or the presence of curves with a very small slope is the sign of the strong turbulent motion.
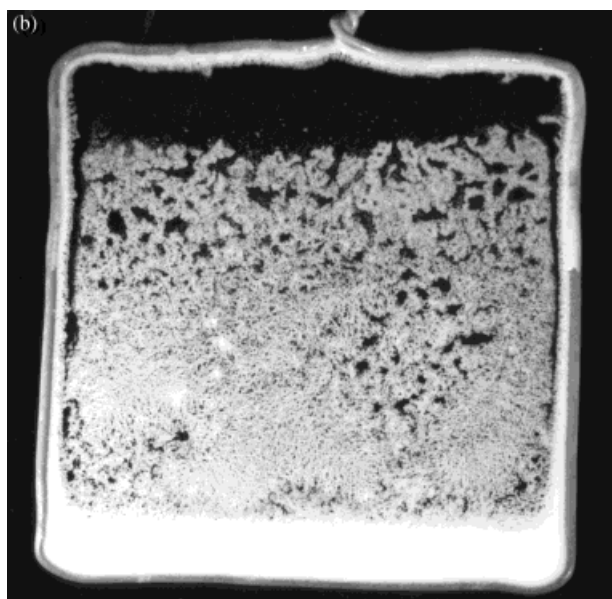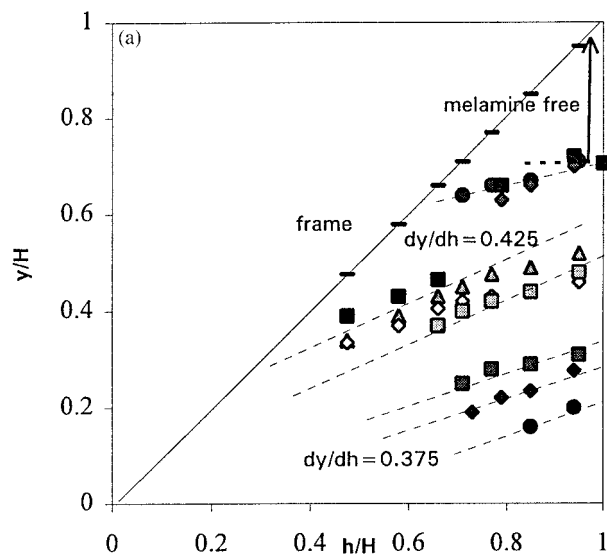

Figure 3 Vertical displacements in film formed from the 0.08 pphp conventional system containing 0.5 pphp melamine 45 μm during frame lifting in frame of 2 × 2 cm with a 0.05 cm/s drawing rate.
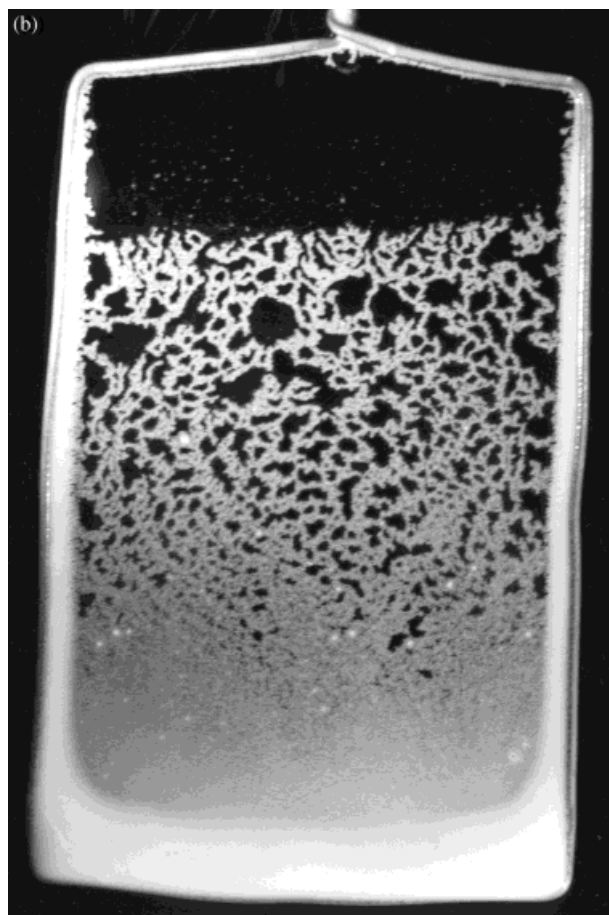
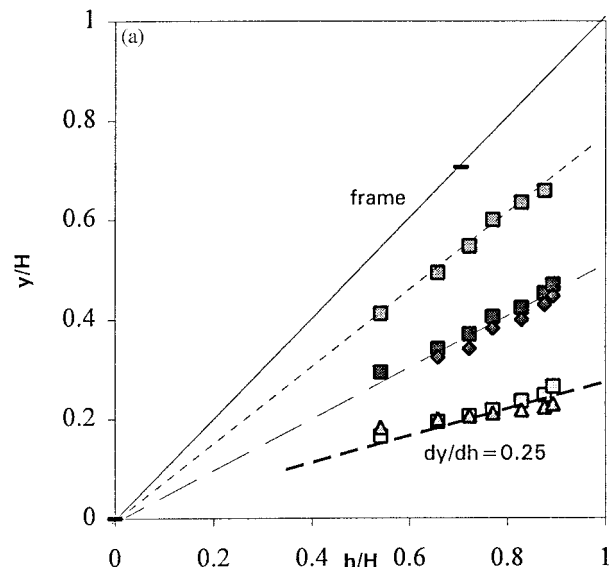## Film Formation

We were interested in the mechanism of film formation and whether the above-mentioned flows can be observed. Therefore, a small amount of melamine ultrafine particles (0.5 pphp) were used
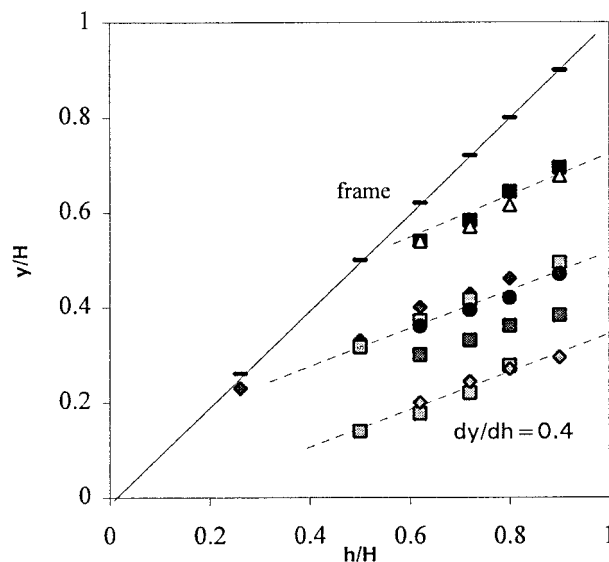
Figure 4 Vertical displacements in film formed from the 0.8 pphp conventional system + 0.5 pphp melamine ultrafine during frame lifting in frame of 2 × 2 cm with 0.03 cm/s drawing rate.

Figure 5 (a) Vertical displacements in the film formed from the 0.08 pphp conventional system + 25 pphp melamine ultrafine during frame lifting in frame of 2 × 2 cm with a 0.03 cm/s drawing rate. (b) Photo of the film formed from the 0.08 pphp conventional system + 25 pphp melamine ultrafine during frame lifting in frame of 2 × 2 cm with a 0.03 cm/s drawing rate.

to detect the motions of the film elements. We assume that the particles in this small concentration will not influence the film-formation properties. The presence of particles in such a small load does not influence the viscosity of the system. The particles' diameters are smaller than the film thickness in every case. Therefore, we may as-

Figure 6 (a) Vertical displacements in the film formed from the 0.8 pphp conventional system + 25 pphp melamine ultrafine during frame lifting in frame of 2 × 3 cm with a 0.05 cm/s drawing rate. (b) Photo of the film formed from the 0.8 pphp conventional system + 25 pphp melamine ultrafine during frame lifting in frame of 2 × 3 cm with a 0.05 cm/s drawing rate.

sume that the particles move together with the film elements.

Film Formation from 0.08 pphp Conventional Systems

Experiments were carried out with a 0.08 pphp surfactant concentration. For a 2×2 cm frame and 0.03 cm/s drawing rate, the upward vertical flow rate in the border [Fig. 1(1)] was found to be 0.05 cm/s and the horizontal flow velocity was 0.03 cm/s. It is important to mention that the vertical flow rate is significantly larger than the velocity of the frame lifting.

Intensive flows were seen in the lower part of the film. Therefore, the motions of the tracer particles could be followed only in the upper area. In the case of a 0.5 pphp melamine load, the traces indicate that the sheet dilates vertically (Fig. 2). Traces with a smaller slope are seen, which must be the result of marginal regeneration at the horizontal meniscus. The rate of the particles in the rising thinner parts at the bottom equals or exceeds the drawing rate (not shown in the graphs). We can see that the regeneration process plays an important role in films formed from the solution of the lower surfactant concentration and the films are dilated vertically.

Experiments were done with *bigger melamine particles* (melamine 45–50) in the case of a 0.5 pphp load (tracer) at a 0.08 pphp concentration. The results are shown in Figure 3. We can see that there is a strong deviation from the straight line with height (h), which can mean that the particles are pushed down to the thicker film regions. Based on the study of Baets[4] in an aqueous solution using styrene beads, we may assume that the film is thinner than 40 μm at the top. It is very possible that bigger particles will not be present in the film; they will be located mainly in the Plateau borders.

Film Formation from 0.8 pphp Conventional System

Films were drawn from the conventional system with a 0.8 pphp surfactant concentration and a 0.5 pphp melamine ultrafine dispersion in different frames (2×2 or 2×3 cm). Different drawing rates were studied. In the case of a 0.8 pphp concentration, 2×2 cm frame, and 0.03 cm/s, the measured upward flow rate in the vertical border is 0.04 cm/s. It equals the rate measured shortly after the end of film formation (Table I).

Only one typical graph is shown in Figure 4 (2

Table II   Film Formation Rates of 0.8 pphp Conventional System with 0.5 pphp Melamine Ultrafine as a Function of Drawing Rate, v

Fame Size (cm $\times$ cm)	v (cm/s)	v_1 [Eq. (1)] (cm/s)	v_r ($= v - v_1$) (cm/s)
2×2	0.03	0.012	0.018
	0.05	0.025	0.025
2×3	0.05	0.011	—

$\times$ 2 cm frame) to represent the character of the film formation. We can see that the traces of particles run linear and parallel with each other, but their slope is smaller than 1. In this case, the horizontal component of the motions is negligible. The new film surface is formed slower from the lower meniscus than the drawing rate, but it behaves as an inextensible membrane: The film elements move together upward. In the case of longer films (2×3 cm frame), the film expanded in the vertical direction in the last third of the drawing time, but the lower $\frac{1}{3}$ part of the film moves as an inextensible membrane.

The rates of film formation at two different drawing rates (v) are calculated from the slopes of curves by eq. (1) and summarized in Table II. In the case of a 2×3 cm frame, this calculation cannot be made because of vertical dilatation taking place between 2 and 3 cm. The rate of v_1 decreases with increasing frame height (2×3 cm). In this case ($v = 0.05$ cm/s), the average rate of v_1 is 0.025 cm/s if the frame is lifted from 1 to 2 cm, but it is only 0.011 cm/s between 2 and 3 cm.

By summarizing our observations, we can say that during the film formation the film dilates horizontally due to the capillary suction of the vertical borders. The thinned film elements rise upward and increase the film area under the upper horizontal bar of the frame. This film pushes the lower sheet downward; therefore, new film is formed from the pool with a lower velocity than the drawing rate. In the case of longer film, significant vertical elongation also can occur.

Effect of a High Load of Melamine on Film Formation

A network formation (see Figs. 5 and 6) was observed in films containing 25 pphp melamine ultrafine particles. This phenomenon will be discussed elsewhere. In the film, melamine-free

spots arise and their movement can be followed. From their displacements, we can study the film-formation properties as mentioned above.

Film Formation at 0.08 pphp Surfactant Concentration

The effect of melamine on the convective motions was discussed for the stationary film. Also, during film formation, the flow rates are smaller in the melamine-filled films than in the melamine-free films.

At a 0.03 cm/s film drawing rate, new film is formed from the pool with a 0.012 cm/s rate in the case of dispersion containing 25 pphp melamine ultrafine (Fig. 5, frame: 2×2 cm). At greater height, the film is likely elongated vertically in a small scale. In some cases, the particles do not move upward in the last part of the film formation, which may be explained by the vertical stretching of the film being above. The upper 25% of the film is melamine-free; there is a sharp border between the melamine-filled and melamine-free film.

Film Formation at 0.8 pphp Surfactant Concentration

By examining the dispersion containing 25 pphp melamine ultrafine particles in a frame of 2×3 cm size (Fig. 6), we can see that at lower height the traces have a smaller slope than in the upper part. The film dilates vertically. The slope of the lower traces is about the same as in the case of a low melamine load and results in $v_1 = 0.010$ cm/s. In the case of the 2×2 cm frame, this type of evaluation cannot be used since the melamine-free spots are formed only in the last 10% of the drawing.

Surfactant Transport During Film Formation

In the previous section, we saw that film formation from the conventional system is ruled by three processes: film formation from the pool, marginal regeneration, and, in some cases, vertical elongation of the film elements. Our observations show that at higher surfactant concentration "without" melamine (0.5 pphp) the film behaves as an inextensible membrane, while at a lower surfactant concentration, the vertical dilatation is more dominant (Fig. 2). Marginal regeneration plays a more important role in films formed from dispersions of lower surfactant concentration.

We can say that the film (in the studied range) is in intensive contact with the borders (Plateau borders); inflow and outflow were seen. Inflow creates a new film part and outflow means film decay. The direction of these processes indicate that marginal regeneration takes place.

Melamine particles make films of low surfactant concentration more rigidlike, while at high concentration, the film formation from the pool is not changed relative to the melamine-free case. The rate of upward flow is slowed down by a high load of melamine at both surfactant concentrations.

In the following section, the surface tension increments are presented which are created on the horizontal surface of the pool by a vertical foam film formation from the pool with different drawing rates. These experiments were done to obtain more information about the mechanism of film formation. From the surface tension increase of the pool caused by film drawing, we can obtain information about the relative surface area increase. We hope to obtain proof of the above-explained film-formation mechanism.

Experiments were carried out at a 0.08 and 0.8 pphp surfactant concentration and a significant difference in behavior was seen. First, we discuss the conventional system with a 0.08 pphp surfactant concentration. After the frame was immersed in the solution, we waited for about 25–30 min until the surface had reached a state close to equilibrium. The results of five experiments can be seen in Figure 7, differing in the rate of drawing. $\Delta\gamma$ $(= \gamma - \gamma_r)$ is the surface tension difference between the surface tension of the pool during (γ) and before (γ_r) film drawing. The surface tension started increasing at the beginning of drawing and it increased continuously in the whole period of film formation. The experiments were carried out with a closed frame, and after lifting, the frame was detached from the liquid. The detachment resulted in 0.1–0.2 mN/m sudden decrease in surface tension (see Fig. 7). In the following time period, a slow surface tension decrease was observed. These observations were explained as follows: At the beginning of the experiment, the surface concentration of the surfactant is not far from equilibrium. The surface area of the system increases if a new surface area is created by forming a vertical film. At the same time, the number of the adsorbed molecules at the pool surface is practically constant, because the adsorption is very slow in this diluted (0.08 pphp) solution. In this way, the surface excess of the surfactant de-
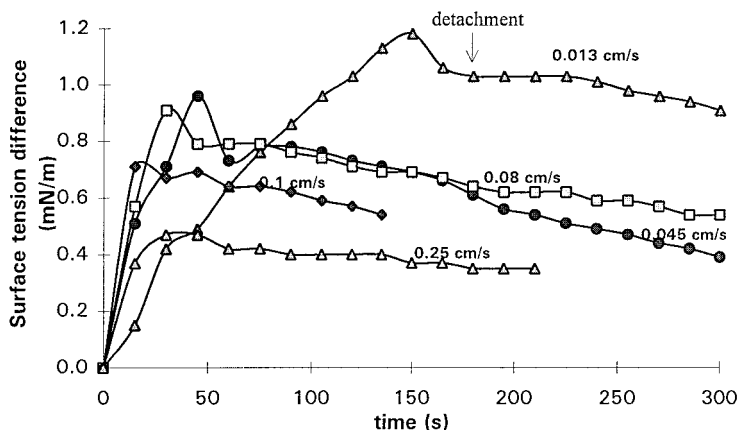
Figure 7 Surface tension change as a function of time at different drawing rates: 0.08 pphp conventional system; 2 × 2 cm closed frame.

creases during drawing and the surface tension increases. After detaching the frame, the contact between the frame and the pool ceases and the meniscus disappears. At this moment, the surface is slightly compressed and the surface tension suddenly decreases by about 0.1 mN/m. From this moment on, the surface tension of the undisturbed surface slowly decreases as a consequence of the slow diffusion of surfactant molecules from the bulk to the surface.

In the formation of a film of 2 × 2 cm size, a part of the surfactant molecules adsorbed on the surface of the pool had flown to the lamella. Therefore, the surface tension of the pool increased. The surface tension difference, read at the detachment point from Figure 7, was plotted as a function of the drawing rate (v) in Figure 8. The results of 2 × 1, 2 × 2, and 2 × 3 cm films are represented in the same figure. We can see from this figure that the higher the rate the lower the increment, $\Delta\gamma$, is. The surface tension difference due to film formation also depends on the surface area change. Figure 8 summarizes the effect of the drawing rate and that of the surface areas on the surface tension increase. The theory of this phenomenon will be presented later.

By repeating the experiments with a 0.8 pphp solution, the measured increments are less than 0.1−0.2 mN/m, indicating that the diffusion is faster. In polyurethane production, a typical dilatation rate is in the range of 0.012−0.017 L/s. A dilatation rate of 0.015 L/s in the production can be compared with our experiments of a 0.05 cm/s drawing rate.

Surfactant Balance of the Film Formation

The surface tension change on the pool was determined in the above-mentioned experiments, but we still cannot calculate the surface area change or the relative surface excess. To determine these quantities, we have to get a relation between surface tension increase and surface area increase. Therefore, separate experiments were carried out to study the surface tension change on a dilating surface. A conventional solution of a 0.08 pphp surfactant concentration was poured into a vessel with a 14.5 cm² surface area (A) and it was left undisturbed for 30 min. The surface tension was measured by the Wilhelmy plate method: γ_r. The
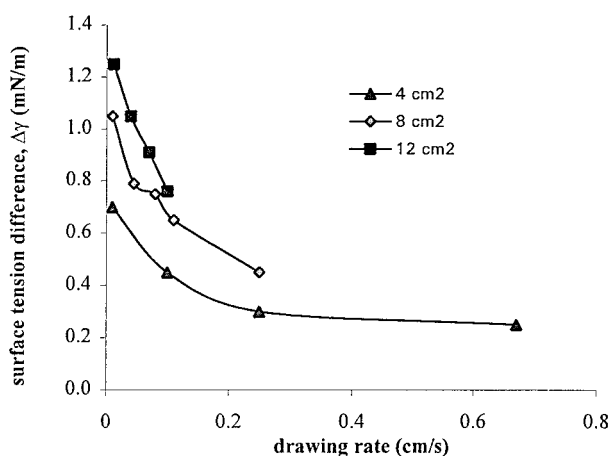
Figure 8 Surface tension change as a function of drawing rate for different surface areas: 0.08 pphp conventional system.

Table III   Surface Tension Increase as a Function of Relative Surface Area Increase

$\Delta A/A$ ± 0.007	$\Delta \gamma$ (mN/m)	Γ/Γ_r
0.067	1.00	0.937
0.133	1.75	0.883
0.200	2.35	0.833

level of the liquid was lowered by sucking a 1, 3, or 5 mL solution using a syringe from the bottom of the bulk. The surface tension was determined again immediately (the measurement takes approximately 10–15 s) and it was larger in every case than γ_r. The surface area of the pool was increased since a wetting, thin film had been created on the wall of the vessel. We supposed that the film surface and the horizontal pool surface are in such an intensive contact that the relative adsorption on them is the same. The adsorption is slow in the case of 0.08 pphp concentration, so we can neglect the adsorption from the bulk to the surface layer in the period of the measurement (15 s). It also means that the surface excess can be taken constant for the whole surface layer. Making this assumption, the mass balance is given then by

$$(A + \Delta A)\Gamma = A\Gamma_r \qquad (2)$$

from which the surface concentration change is given by

$$\frac{\Gamma}{\Gamma_r} = \frac{1}{1 + \Delta A/A} \qquad (3)$$

where A is the surface of the pool; ΔA, the surface area change, and Γ_r and Γ, the surface concentration before and after the film formation, respectively (Table III).

In this way, we have an empirical relation between surface tension change and relative surface concentration. This function must be independent of the manner of dilatation and can be used to calculate the relative surface concentration change of the pool surface during foam film formation.

The concentration of the pool surface decreases because the adsorbed surfactant flows (with its surface or by diffusion on the surface) to the surface of the film. We have seen from the tracer experiments that only a part of the lamella is cre-

ated from the pool; the pool surface does not expand parallel with the film formation.

From the surface tension measurements caused by the film formation (Table IV, column 3), we can estimate how large the homogeneous surface area increase is that would result in the given surface tension increase. The calculations were done and the calculated surface area increase, ΔA (Table IV, column 4), was compared with the surface area of the film, A_{film}. It is seen that the surfactant concentration on the lamella is only 5–15% of that on the pool surface. The smaller the surface area of the film and the slower the drawing, the larger the ratio $\Delta A/A_{film}$.
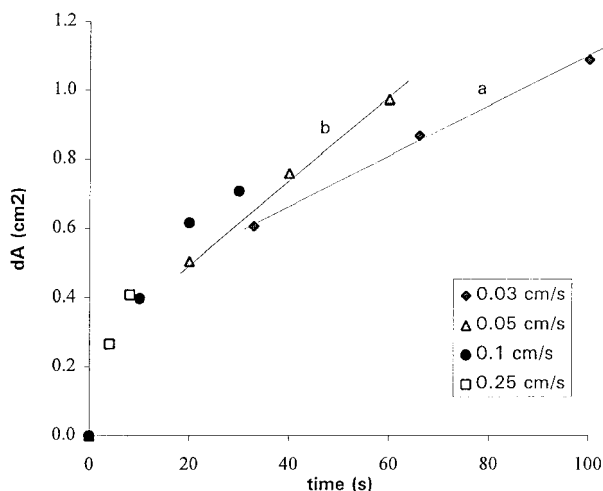
By plotting ΔA against the drawing time, we see that the measured points result in saturation curves (Fig. 9) for every drawing rate. The curves run more or less together until about 0.3 cm^2, so it seems that the frame lifts a small film independent of drawing rate and then the surfactant flows to the film with constant velocity. The dA/dt surface flow rate can be read from the straight parts of curves (a) and (b) of Figure 9, and by dividing dA/dt by the width of the film (2×2 cm = 4 cm), we get the rate of expansion, v_A (Table V). This velocity shows the rate by which the pool surface would expand to the direction of the film if the coverage on the expanding film and on the pool were the same.

By summarizing the experimental results,

1. The expansion rate (v_A) is independent of the height of the lamella (so on the age of the

Table IV   Average Elongation ($\Delta A/A_{film}$) Calculated from Empirical Relation L = 4 cm, A = 14.5 cm^2

v (cm/s)	A_{film} (cm^2)	$\Delta \gamma$ (mN/m)	ΔA (cm^2)	$\Delta A/A_{film}$
0.03	4	0.65	0.605	0.151
	8	0.90	0.866	0.108
	12	1.10	1.088	0.091
0.05	4	0.55	0.505	0.126
	8	0.80	0.758	0.095
	12	1.00	0.972	0.081
0.1	4	0.44	0.397	0.099
	8	0.66	0.615	0.077
	12	0.75	0.706	0.059
0.25	4	0.30	0.265	0.066
	8	0.45	0.408	0.051
	12	Rupture	—	—

Figure 9 Calculated surface area increase as a function of time at different drawing rates.

film) at slow drawing rate in a certain time range.

2. The expansion rate increases with increasing drawing rate.
3. The expansion rate is negligibly small in comparison with the drawing rate.

We suppose that the film is freshly formed above the meniscus, as it is pulled out from the bulk between the surfaces of the meniscus (Plateau border). In this case, a large surface tension difference exists between the lamella and the pool; therefore, the surface active agent transport most probably occurs by the Marangoni flow. The expansion rate is then the rate of the Marangoni flow. The film-formation rate is less than the drawing rate (see Table V), resulting in a viscous flow (Frankel theory) additionally to the above-mentioned Marangoni flow. These transports increase the rate of expansion.

The surfactant (although the amount is small) flown from the pool's surface to the film must play a role in the stabilization of the film. The film ruptures if the drawing rate exceeds a critical value, when the $\Delta A/A_{film}$ is lower than 0.05. Polyurethane production can be compared with a 0.05 cm/s drawing rate ($\Delta A/A_{film} > 0.05$; see Table IV), where rupture does not occur in the period of drawing. At a larger surfactant concentration, the film is stabilized by the adsorption from the bulk and decreases the Marangoni effect.

Effect of Melamine

The results performed with melamine dispersions (25 pphp) differ significantly from those obtained with solutions without melamine (Fig. 10). In the beginning of the frame lifting, the surface tension of the pool increases to a higher value and stays there up to the end of film formation. After detaching the frame from the surface, the surface tension decreases to the initial value. In the pool, there is no mark of previous film formation at both surfactant concentrations. In these cases, the maximal surface tension differences (the first two or three points were omitted) existing during film lifting were taken and are collected in Table VI. It can be seen that within the experimental error this surface tension increase is independent of the size of the film and the drawing rate, but it differs for the different surfactant concentrations. It was shown[15] using rheological measurements that there is interaction between the particles and that they can be built into the surface layer. A concentrated network of particles causes the surface tension to increase significantly if the surface area is enlarged, since the network is in a strained state. After reaching a certain surface tension difference, further dilatation is not possible: The surface "ruptures." This point can be interpreted as a special "yield point": From this value on, parts of the surface are strained (larger surface tension) and other parts of the surface continuously dilate and flow.

The difference in the maximal surface tension for the two different concentrations can be explained by the fact that the rate of adsorption depends on the surfactant concentration. The larger surface tension difference may exist at 0.08 pphp because the adsorption is slower.
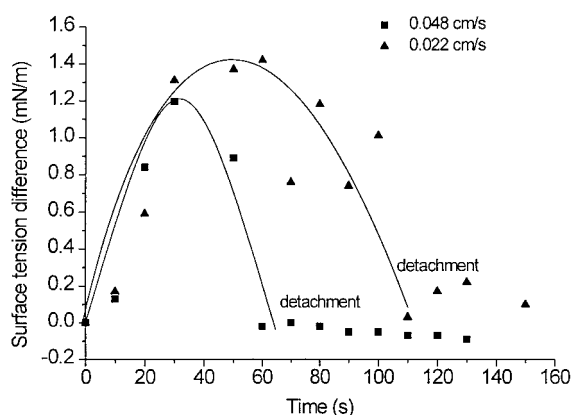
CONCLUSIONS

Convective currents in vertical liquid films are observed by a tracing method. During film drawing, a fast upward streaming [Fig. 1(1)] is observed in the borders parallel to the vertical me-

Table V Expansion Rate as a Function of Drawing Rate

Drawing Rate v (cm/s)	0.03	0.05
Expansion rate v_A (cm/s)	0.0018	0.0029
v_A/v	0.060	0.058
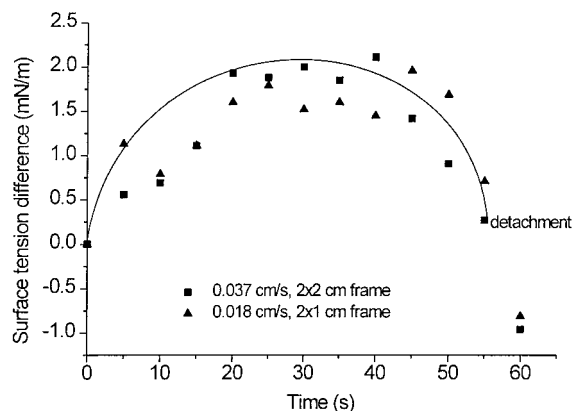
a.

b.

Figure 10 Surface tension increase as a function of time for different surfactant concentrations: (a) 0.08 pphp Tegostab BF 2370 + 25 pphp melamine superfine/Voranol CP 3322; (b) 0.8 pphp Tegostab BF 2370 + 25 pphp melamine superfine/Voranol CP 3322.

nisci. Under the upper part of the frame, the stream slows down and turns toward the middle (2) and downward. The middle part of the film moves diagonally downward compared to the frame and dilates toward the vertical legs of the frame (3). Essentially, two vortices are formed rotating in the opposite direction. These movements interfere with large rising thin film parts that originated from the lower horizontal meniscus (4). At the same time, the fluid flows downward in the vertical menisci (5). Obviously, this fluid had flown out of the film, causing thinning.

It is very probable that the observed processes are driven by gravity. The gravitational force

maintains the negative pressure in the menisci, which forces the liquid to flow toward the menisci.

The adsorbed surfactant makes the film stable. The surfactant transfer during film formation was followed by surface tension measurements on the pool. The surfactant transfer onto the film surface can take place by surfactant adsorption from the bulk of the film to the surface and by surface diffusion from the pool to the film.

The rate of surfactant adsorption is slow in diluted solutions (0.08 pphp); thus, in these cases, the adsorption can be neglected and the rate of surface diffusion can be investigated. Films were formed from 0.08 pphp surfactant solution with different velocities. The changes in the surface tension of the pool were measured and the surface excess change caused by the diffusion of the surfactant from the surface of the pool to the surface of the film were calculated. This quantity was found to be only a few percent of the surface excess necessary for equilibrium coverage. The rate of surface diffusion depends on the velocity of frame lifting and is independent of the length of the film at certain drawing rates. From these experimental facts, it was concluded that the force pulling the surfactant toward the film is partly viscous and partly capillary force due to the surface concentration differences between the pool and the surface of the film.

The low rate of surface diffusion showed that the fresh film surface is nearly independent of the pool surface and the meniscus behaves as a slit, producing a film with a nearly surfactant-free surface. At larger surfactant concentration, melamine-free films behave as inextensible films, while the decrease of surfactant concentration results in more pronounced vertical dilatation.

Two characteristic phenomena were observed during film formation from suspensions containing 25 pphp melamine ultrafine:

1. The convective currents are slower in the melamine-filled film than in the corresponding melamine-free lamellae. This may be caused mainly by the increased viscosity.
2. No surface tension difference was seen on the surface of the pool after film formation. It seems that the melamine hinders the surface diffusion.

The rate of diffusion is slow; nevertheless, it plays an important role in film stabilization when surfactant concentration is low (e.g., 0.08 pphp or less) or surface diffusion is hindered by the

Table VI   Results of Surface Tension Measurements in the Period of Film Formation

Surfactant Concentration (pphp)	Drawing Rate (cm/s)	Frame (cm × cm)	$\Delta\gamma$ on the Pool (mN/m)	No. Experiments	Maximal Deviation (mN/m)
0.08	0.010	2 × 2	2.5	2	0.5
	0.018	2 × 1	2.0	2	0.2
	0.037	2 × 2	2.0	1	—
	0.050	2 × 1	2.3	2	0.3
	0.080	2 × 2	2.6	3	0.5
	0.100	2 × 1	2.0	1	—
0.8	0.022	2 × 2	1.4	2	0.3
	0.048	2 × 2	1.1	3	0.2
	0.065	2 × 2	1.6	2	0.3
	0.090	2 × 2	1.6	1	—

presence of melamine particles. This effect can be experienced at high velocities of film drawing: The films rupture the higher the drawing rate is, the lower the surfactant concentration is, or the higher the melamine concentration is. The effect of melamine can be compensated by increasing the surfactant concentration.

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