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# Avoiding surface instability and slurry jamming in simultaneous multilayer coating of structured particulate films

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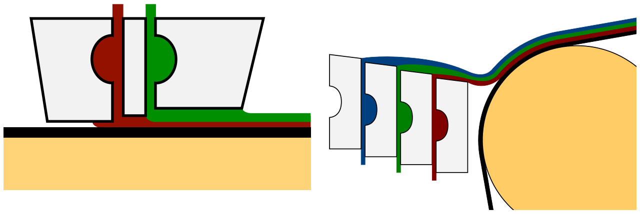
## Abstract

Simultaneous multilayer coating techniques are widely known, but their industrial application remains limited to narrow market sectors. One barrier to adoption may be the mismatch between industries that are familiar with such processes but have no need, and industries that have need but are not familiar. Moreover, there are application-specific technical challenges to developing multilayer coating processes. In this article we describe our resolution of two specific issues in simultaneous multilayer coating of all-aqueous highly loaded slurries for new and emerging energy applications. The first issue is particle jamming (associated with shear thickening) of the highly loaded slurries in the die internals, which we alleviated by adding small amounts of viscosity modifiers without reducing the solid loading. The second issue is a Marangoni-driven surface instability that resembles top layer de-wetting, which we solved by carefully selecting surfactants to tune the dynamic surface tensions of each slurry. Both issues were resolved early in a step-wise development, saving significant development cost which in our case was driven by expensive materials.

## Introduction

Advanced materials for applications such as energy are increasingly reliant on functional materials in the form of structured films that may be heterogeneous and/or multilayered, often requiring distinct stratification, intimate inter-layer contacts, controlled and graded morphologies, and thin individual layers. For both new technology development and deployment, it is critical to be able to rapidly prototype and cost-effectively manufacture such films at-scale. Traditional prototyping and manufacturing methods for multilayer structures are cumbersome, requiring individual coating and careful handling of many thin constituent layers before laminating them all together.

In contrast, coating processes such as multilayer slot and slide coating (Figure 1) are attractive as ‘next-generation’ options with the potential for reducing the complexity and cost of both prototyping and manufacturing by consolidating multiple individual fabrication steps into a single wet-on-wet coating step. Lamination processes would consequently be eliminated, along with sacrificial material costs such as liners. Moreover, multilayer coating can produce thinner individual layers than can be achieved one layer at a time by broadening the coating operability windows [1].



(a) (b)

**Figure 1. Schematic of dual layer slot (a) and multilayer slide (b).**

Saint-Gobain is exploring for its diverse business sectors the broader application of simultaneous multilayer slot and slide coating techniques to different material systems. One particularly well-suited application is an internally developed all-ceramic solid oxide fuel cell (SOFC) [2]. The SOFC “stack” architecture comprises an electrolyte “heart” component with 6 functional ceramic layers (Figure 2). The individual layers range in thickness from < 5µm to > 100µm and are traditionally produced by a series of independent knife coating (tape casting) steps followed by punching, lamination, and individual quality control (QC).

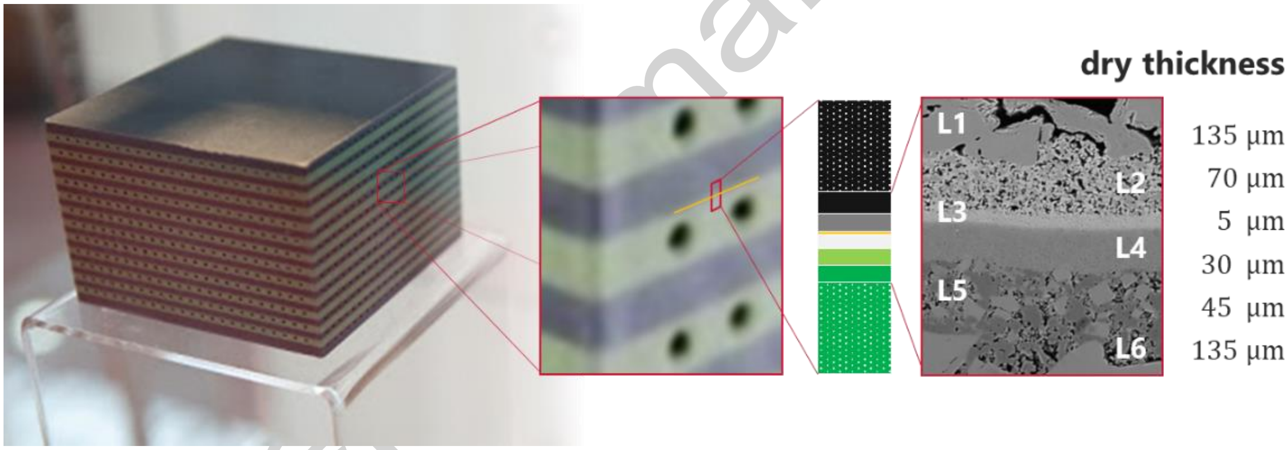


**Figure 2. All-ceramic SOFC stack structure illustrating the 6-layer electrolyte “heart” component. The architecture has an engineered microstructure with various thicknesses and porosity levels**

**The “heart” component has 6 layers, the coating liquid formulations are all water-based (fully miscible wet miscible wet layers with nominally no interfacial tension), and the casting and handling of the thin tapes can tapes can be very challenging. All of these features render “heart” fabrication amenable to simultaneous simultaneous multilayer coating.**

Figure 3 illustrates the process simplification that could be realized by changing the fabrication paradigm from single layer to simultaneous multilayer coating.

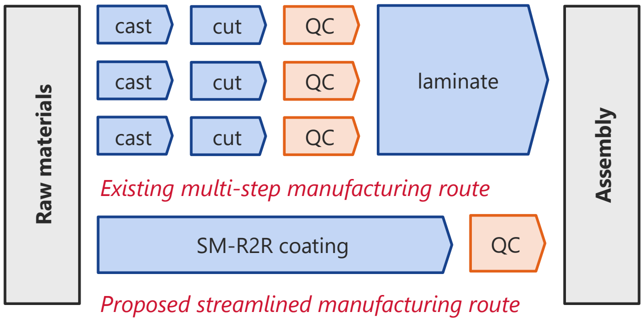


**Figure 3. Simultaneous multilayer coating can consolidate and streamline existing multi-step manufacturing routes, thereby enabling rapid development and continuous, at-scale manufacturing of multilayer devices.**

We partnered with the Department of Energy (DOE) Advanced Manufacturing Office (AMO) in 2017 to explore multilayer slot and slide coating for industrialization not only of SOFC components, but also other multilayered structures of interest to the DOE such as photovoltaics, lithium-ion batteries, and capacitors. We initially identified three key platform elements for the development of simultaneous multilayer coating processes:

1. **Coating liquid (ink) formulation** (e.g., particle loading, binders, additives)
2. **The SM coating process** (e.g., die design, line speed, die gap settings)
3. **Drying and solidification** (e.g., temperature, humidity, convection rate)

All platform elements interact with each other. For example, formulation details such as solids loading influences both coatability windows (via viscosity together with die configuration and line speed) and drying capacity.

Many of the challenges to address these elements are well-known in the literature and industry. The photographic film industry developed simultaneous multilayer coating processes over half a century ago, but much of the knowledge and expertise in the closed literature were lost with its decline. Some general features of the simultaneous multilayer coating process and the physical phenomena limiting the stable coating operability windows remain under scientific investigation at the time of this writing. Some recent studies continue to revisit slot coater operability and slide flow instability [3, 4], both of which are largely influenced by viscosity, and the latter also by interfacial tensions. Another important line of investigation is on the compatibility between the wet liquid film layers themselves [1, 5-7].

We were able to address many of these considerations systematically in simplified lab/pilot situations by adopting a step-wise development, namely by starting with batch single layer slot coating trials, moving to roll-to-roll single and dual layer slot trials, and finally engaging in multilayer slide trials. By addressing various single-layer formulation issues and pair-wise compatibility issues in the context of simpler and smaller trials, we significantly reduced development costs, which in our case was driven by expensive raw materials.

We now focus on two formulation/process issues—one each during the single-layer and dual-layer coating trial phases to highlight the successes of our step-wise approach—which we believe are both generally relevant for potential adopters of multilayer coating techniques. We also believe that both issues involve some interesting fluid mechanical phenomena that may warrant more scrutiny from the scientific community and/or translation of existing academic literature of fundamental phenomena into more applied form.

These issues are: (1) jamming of the highly loaded slurries in the die internals associated with shear thickening, and (2) a surface instability that resembles top layer de-wetting.

## Slurry jamming associated with shear-thickening

Unlike the incumbent self-metered knife coating (tape casting) process, the pre-metered slot coating and slide coating processes both require precision pumping and flow through narrow clearances such as tubes and die internals. Therefore, from the outset we were concerned about the high solids loading in the slurries and the role of shear-sensitive viscosity that may challenge these requirements.

Rheological characterization of all the incumbent slurry formulations revealed that one of the formulations exhibited shear-thickening in a standard shear rate sweep (Figure 4a). We conducted a batch mode single layer slot coating trial for this shear thickening slurry. The slot exit gap of 500 μm and flow rates such that average velocity in the was 20 cm/s, and the die-web gap was 200 μm with web speed of ~1.7 cm/s. Rough calculations based on Newtonian flow kinematics indicate wall shear rate in the slot on the order of 50 $s^{-1}$ and shear rate in the die-web gap on the order of 100 $s^{-1}$. These shear rates fall in the range of the onset of shear thickening according to Figure 4, suggesting that the slurry may exhibit shear-thickening during our coating process, and thereby result in coating issues.

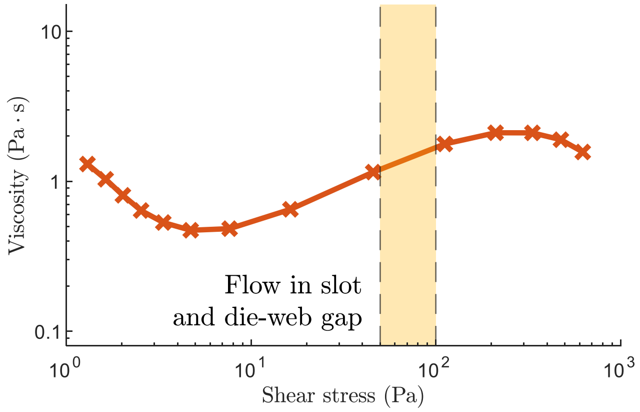


**Figure 4. Shear viscosity of the original shear thickening slurry, measured on a DHR-1 rheometer with CC28 cup-and-bob geometry at 25°C.**

Indeed, the coating trial was plagued by non-uniform and non-constant flow out of the exit slot due to agglomerated clumps issuing from the die exit. We did not observe agglomerated clumps or slot exit flow non-uniformities for the other (strictly shear-thinning) slurries of comparable viscosity ranges. These observations suggested jamming of particles that may be associated with the shear-thickening phenomenon.

### *Relevant literature on shear-thickening*

Shear-thickening is commonly observed for suspensions of solid particles in liquids. It typically occurs only above a critical shear stress at high solid volume fraction [8], and is commonly attributed to either or both of two phenomena: hydrocluster formation [9] and contact friction [10, 11]. It is possible that both mechanisms participate in shear-thickening, but it has been suggested that hydrocluster formation may explain continuous shear-thickening such as observed in our slurry, whereas contact friction may explain the more “extreme” discontinuous shear-thickening [10]. Both mechanisms suggest that jamming issues may be associated with shear-thickening viscosity.

The trial results with clumping (jamming), together with these potential mechanisms, suggest that it may be necessary to suppress shear-thickening for slot/slide coating of highly particle-loaded slurries. Both experiments and theory suggest that there is a threshold solid loading below which the shear-thickening effect is not observed, so that issues may be mitigated by reducing the solid loading (dilution). However, it is not desirable to lower the solids loading because such dilution would increase the drying load required.

There are many investigations of shear-thickening particulate suspensions in the literature, but few of them discuss how to eliminate the phenomenon by means other than reducing the solid loading by dilution. Nor is there much literature on the influence of other additives on the phenomenon of shear-thickening, particularly that of non-particulate and non-associative viscosity modifiers (viscosifiers). We have found only two studies suggesting that shear-thickening in suspensions can be “masked” by other rheological phenomena.

Brown, et al.[12] found that yield stress can mask shear-thickening in a glass sphere suspension: actually, rather than masking shear-thickening by imparting yield stress, they un-masked the effect by adding surfactants to eliminate the yield stress behavior of their unmodified suspension. Reversing their finding, we may be able to mask shear-thickening by endowing our slurry with yield stress behavior, but that may incur the cost of potentially more/different practical coating challenges—indeed the role of dispersants in our incumbent slurry formulations likely serve to prevent phenomena such as aggregation and yield stress behavior in the first place.

A study by Orawiec, et al.[13] found that adding a non-associative viscosifier (polypropylene glycol diacetate) in large enough concentration into a highly loaded silica suspension of propylene glycol masked the underlying shear-thickening behavior of their suspensions.

### *Elimination of shear-thickening and jamming*

Motivated by the finding of Orawiec, et al.[13], we remove the shear-thickening by reformulating the slurry with the non-associative viscosifiers methyl cellulose (MC) and a proprietary additive denoted RT, which is similar to MC. We also included a formulation with a large loading of surfactants on the premise that shear-thickening was related to contact friction and that more adsorbed surfactant may “lubricate” the particles. The modified recipes are summarized in Table 1.

Table 1. Reformulation attempts to suppress shear thickening.

| | **original** | **RT** | **Methyl Cellulose** | | **surfactant** |
|---|---|---|---|---|---|
| | | **+0.5%** | **+0.25%** | **+0.5%** | **+25%** |
| water | 19.84 | 19.75 | 19.79 | 19.74 | 19.78 |
| binder | 10.91 | 10.86 | 10.88 | 10.85 | 10.87 |
| surfactant | 1.69 | 1.69 | 1.69 | 1.69 | 2.05 |
| powder solids | 67.56 | 67.23 | 67.39 | 67.22 | 67.30 |
| thickener | 0.00 | 0.48 | 0.24 | 0.50 | 0.00 |
| liquid/powder solids | 0.319 | 0.319 | 0.319 | 0.319 | 0.324 |

The shear viscosities of the original and modified formulations are compared in Figure 5. The RT and MC viscosifiers both shift the overall viscosity up—as expected by their functionality—and appear to alleviate the shear thickening. In contrast, the added surfactant shifted the overall viscosity down and preserved the shear-thickening.

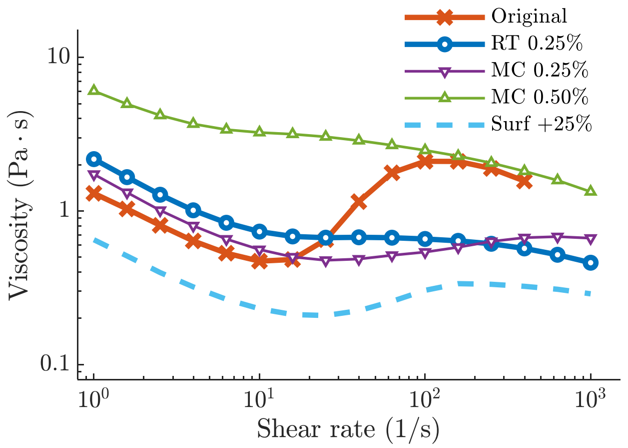


**Figure 5. Shear viscosity comparisons for various reformulations of our shear thickening slurry in terms of shear rate. All measurements done on DHR-1 rheometer with CC28 cup-and-bob geometry at 25°C.**

### *Discussion of slurry jamming and rheology*

The onset shear stress for shear-thickening (location of minima in Figure 5 bottom) of the modified formulations compared to that of the original formulation may inform hypotheses about the mechanisms behind alteration of the shear viscosity profile. Nakamura et al. [14] showed that changes in solid loading and solvent viscosity do not change the onset stress but changes in particle size do. Figure 6 recasts the shear viscosity curves of Figure 5 in terms of shear stress. The onset stress for shear-thickening for the extra surfactant loaded formulation does not shift appreciably. In contrast, both the viscosifier additives shift the onset stress for shear-thickening to the right, suggesting that their role may not be limited to simple viscosity modification of the solvent, and that there may be an associative effect which changes the effective particle size. Moreover, the RT more effectively suppresses the shear-thickening than does MC at the same loading, although this is also true of the general efficacy for increasing the base viscosity (as measured by the shift at low shear rates).

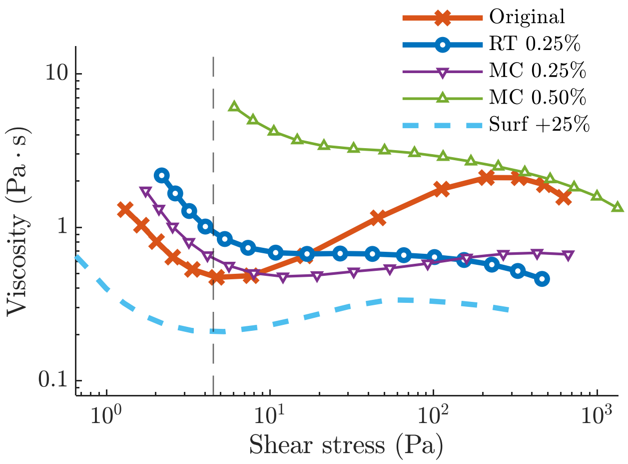


**Figure 6. Shear viscosity comparisons for various reformulations of our shear thickening slurry in terms of shear stress. Dashed vertical line shows onset of of shear-thickening of original formulation, which lines up well with that of the surfactant modified formulation.**

Because both of the viscosifiers are classified as non-associative, their effect of shifting the critical onset stress and of suppressing the shear-thickening behavior is unexpected. Moreover, both viscosifiers were added in small amounts, $< 0.5\%$, in contrast to the relatively high viscosifier loadings ($> 20\%$) reported by Orawiec, et al.[13] to mask shear-thickening.

Therefore, we have no compelling explanation of the effect, which if novel may merit further study. Such a study could serve the practical pursuit of eliminating shear-thickening by means other than reducing the solid loading, which could improve coating processability without negatively impacting other practical considerations such as drying capacity.

In any case, the non-shear-thickening formulation with small amount of RT presented no issues of jamming during coating trials, suggesting that simplistic correlation between “shear-thickening” and “jamming” may be a sufficient paradigm for rheology tuning to avoid coating instability, as long as there are no other difficulties with coatability or coating defects.

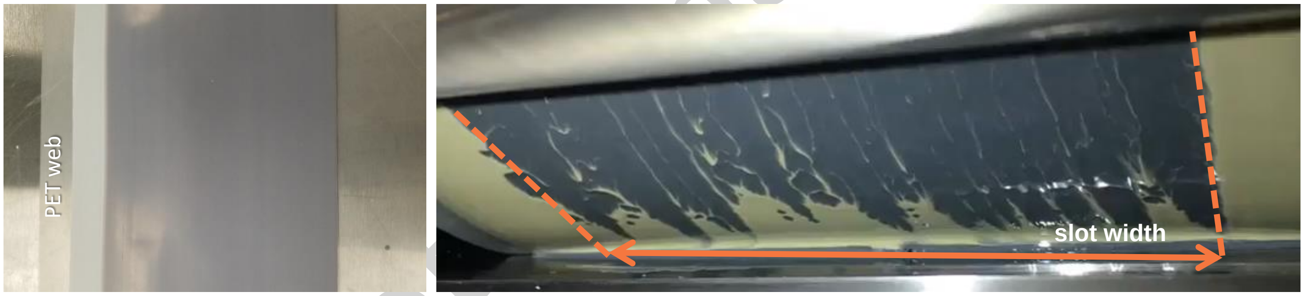
## Surface instability resembling top layer de-wetting

In general, two liquids deposited one onto another may exhibit instability manifesting as the top layer retracting, or appearing to retract, from the bottom layer into itself. For example, Figure 7 compares the same two aqueous fully miscible slurries when deposited in different orders: the black slurry appears to effectively wet (spread) on the gray slurry, but the gray slurry appears to de-wet (retract) from the black slurry.


(a) (b)

**Figure 7. The same two slurries deposited on a surface in different orders. (a) the black slurry appears to spread stably upon the gray slurry, but (b) the gray slurry retracts on itself when deposited upon the black slurry.**

In our dual layer slot coating trials, layer pairs whose drop-on-drop experiments look like Figure 7a yielded stable coatings with good outcomes (Figure 8a). Conversely the surface instability with the drop-on-drop experiment in Figure 7b manifests as a coating instability immediately downstream of the slot coating bead (Figure 8b).



(a) (b)

**Figure 8. (a) Dual layer slot coated bilayer film without surface instability. (b) Surface instability during dual layer slot coating.**

When the liquids are immiscible and separated by true phase interfaces, the retraction is described as de-wetting. When the liquids are completely miscible, there is no true interface at which liquids may wet or de-wet; nevertheless miscible multilayer films may still suffer a surface instability such as driven by the Marangoni phenomenon [6] that may resemble de-wetting in appearance. In either case, interfacial phenomena are important factors that determine the compatibilities of the adjacent liquid layers with respect to either of these phenomena during multilayer coating.

The following sections will detail a chain of ideas to motivate our resolution of the instability illustrated in Figure 8b. The spreading arguments between immiscible layers motivates the oft-cited surface tension grading rule, which is typically invoked even in situations where the layers are fully miscible and where the Marangoni phenomenon is the more likely explanation for surface instability. Surface tensions of the individual layers per se are not relevant in the fully miscible case, but they indirectly indicate other conditions that determine the Marangoni instability, for example differences in the surfactant concentration between the layers that could drive interlayer diffusion. Therefore, surface tension grading—specifically dynamic surface tension—could still be a useful albeit imperfect rule of thumb to avoid surface instability in miscible systems.

Hereafter we mean "surface tension" of a liquid to imply its "surface tension with air", and will distinguish surface tensions between adjacent layers as "interfacial tensions".

### ***Spreading and the surface tension grading rule***

Equilibrium thermodynamic arguments predict that liquid films cast upon an underlying liquid film will tend to remain spread as a film when the spreading coefficient $S$ is positive, and retract ("de-wet" from the underlying liquid film) when it is negative; the magnitude of $S$ corresponds to the readiness of spreading and de-wetting [1, 5, 15]. The spreading coefficient $S$ is defined in terms of the work of adhesion $W_A$ between the liquids, and work of cohesion $W_C$ of the liquid being spread, i.e., the top layer [15]:

$$S \equiv W_A - W_C \tag{1}$$

In practice, these energies can be expressed in terms of the measured interfacial tensions $\sigma_b$, $\sigma_t$, and $\sigma_{t,b}$, respectively the surface tensions of the bottom and top liquids and interfacial tension between the two liquids:

$$S = \sigma_b - \left(\sigma_t + \sigma_{t,b}\right) \tag{2}$$

For liquids with measurable interfacial tension $\sigma_{t,b}$, the spreading coefficient $S$ are shown to be a good indicator for stability against de-wetting of top layers upon bottom layers in two-layer slide coating experiments [5]. For negligible interfacial tensions $\sigma_{t,b}$, the spreading coefficient reduces to a comparison of the individual surface tensions $\sigma_t$ and $\sigma_b$ of each layer with the air, with the spreading criterion $S > 0$ becoming $\sigma_b > \sigma_t$.

This criterion is the basis for the oft-cited surface tension grading rule for multilayer coating[1, 5], which states that each layer's surface tension between its coating liquid with air should decrease in value from the bottom of the multilayer (touching the web) to the top of the multilayer (exposed to air). Buerkin, et al.[5] have recently verified in simultaneous multilayer coating experiments of immiscible layers that the surface tension grading rule must be augmented to include the interfacial tensions $\sigma_{t,b}$ between the layers to full spreading parameter criterion.

### ***Marangoni-driven self-thinning film flows***

When considering multilayer coating of miscible liquids, it is at first unclear what role, if any, is played by surface tensions. Clearly, the bottom layer must sufficiently wet the substrate, and so its surface tension does have a bearing on how well it wets the web on startup when it is exposed to air. However, the notion of interfacial tensions among the layers is nonsensical because there are no interfaces between the various subsequent liquid layers, and so it is the role of the surface tensions of each layer with air lose their meaning in the context of spreading. A framework for understanding the role of surface tensions is provided by Marangoni flows and the corresponding instability or potential for self-thinning behavior associated with diffusible surface-tension-depressing species.

Horiuchi, et al.[6] studied simultaneous dual layer slot coating of miscible bilayer systems, specifically a surfactant-laden aqueous layer upon an alcohol layer, in which they observed “top layer de-wetting”. Despite their use of the term “de-wetting”, they did not invoke any spreading arguments but rather posited the following Marangoni phenomenon driven mechanism. A surface-tension-depressing species (in this case the alcohol) diffuses into the top layer from the bottom layer and locally depresses the top layer’s surface tension, setting up lateral surface tension gradients that pull liquid away from the regions of low surface tension. Such thinned regions will preferentially be further enriched with alcohol from the lower layer because of the shorter distance to travel, and thus set up a positive-feedback self-thinning lateral film flow (Figure 9). It is stated that the instability should then be more readily initiated if there are pre-existing nonuniformities in the thickness of the top layer [6], such as by other types of coating instabilities like ribbing.

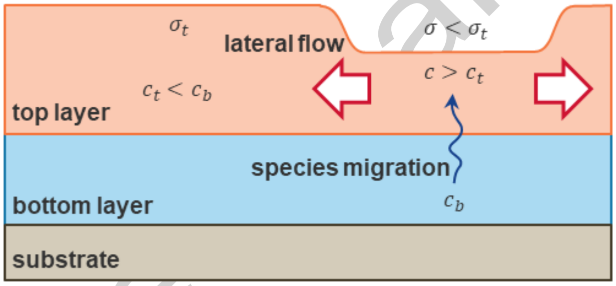


**Figure 9. Schematic of surface tension gradient driven film thinning flow in the top layer, induced by locally elevated concentration of surface tension modifying species that diffused from the bottom layer. The overall species concentration $c_t$ in the top layer is lower than that in the bottom layer, $c_b$. The species consequently diffuses from the bottom layer into the top layer and locally increases the species concentration $c$ at the top layer surface. The surface tension $\sigma$ there is consequently depressed relative to the surrounding surface tension $\sigma_t$, inducing flow away from that locality. Due to the shorter diffusion distance there, the thinned film surface is further enriched in the species relative to the surrounding surface, further increasing the surface tension gradient in the plane of the film and accelerating the lateral flow in a positive feedback that leads to a self-thinning flow that looks like a retraction or apparent “de-wetting”.**

The argument works just as well for any surface-tension-modifying species in the bottom layer that has potential to diffuse through the top layer onto the film surface, such as surfactants from an aqueous bottom layer as in our case.

### *Relationship between surface tension grading and Marangoni instability*

In general, awareness of the Marangoni phenomenon motivates the formulation of low surface tensions in the top layer, contrary to high surface tension to promote film leveling. Intrinsically low surface tensions in the top layer prevent large surface tension gradients from developing due to contamination from the environment as well as diffusing species from below, and hence renders the coating less sensitive to Marangoni defects.

This idea is clearly compatible with the surface tension grading rule, albeit for different reasons than motivated by the thermodynamic spreading coefficient arguments, which are not applicable between miscible liquids. Nevertheless, examples and explanations in the literature typically apply the surface tension grading rule to fully miscible systems [1, 7], presumably with success. This may be explained in some specific cases where the surface tensions of each layer straightforwardly represents the potential for diffusing species in the bottom layer to locally depress the surface tension in the top layer.

A simple example is two solutions with the surfactant Makon UD-6 (Stepan) in different loadings. Figure 10 shows a model liquid bilayer coating (hand draw down) from aqueous solutions of methylcellulose and UD-6, differing only in the concentrations of surfactant and type/amount of coloring dye (which is not surface active). Loadings of the surfactant are compared in units of the critical micelle concentration (CMC): is 0.1 × CMC in the orange bottom layer and 10 × CMC in the blue bottom layer.

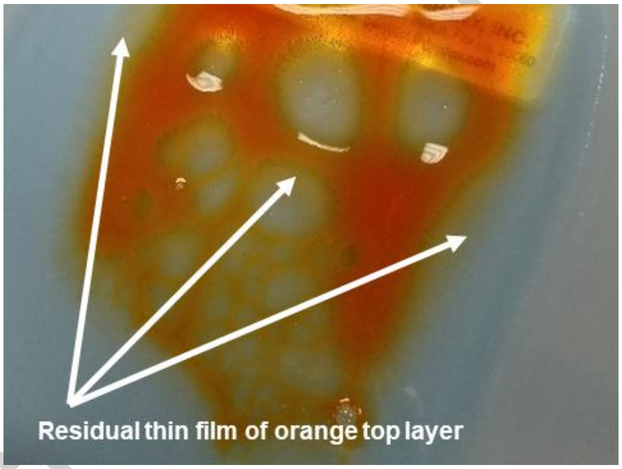


**Figure 10. Bilayer hand draw down coating of model aqueous liquid colored with dyes with different loadings of the surfactant Makon UD-6 (Stepan): $0.1 \times$ CMC and $10 \times$ CMC respectively in the orange top layer and blue bottom layer. Both solutions are viscosified with enough methylcellulose to raise the viscosity to $2\mathrm{Pa} \cdot \mathrm{s}$. The apparently "de-wetted" zones retain an orange tinge indicating that the top layer has only thinned rather than actually de-wetted from the bottom layer.**

Because the dilute top layer concentration is below CMC, its surface tension is higher than that of the bottom layer, and the surface tension grading rule is violated. It is the surfactant concentration difference that drives the instability via the Marangoni phenomenon, and the  surface tension grading violation is only a consequence of that concentration difference. But the converse is not necessarily true: if the surface-tension-depressing species were not the same in the top and bottom layers, different surface tensions would not necessarily imply a potential for diffusion or surface tension depression of the top layer.

Indeed, the experiments of Horiuchi, et al.[6] are largely inconsistent with the surface tension grading rule: instability was observed in most cases even as the top layer aqueous surfactant solution had a lower [equilibrium] surface tension than the bottom alcohol layer. This observation illustrates an important deficiency in the discussion so far which has relied on measurements of equilibrium surface tensions: the Marangoni phenomenon includes dynamics of diffusion through the liquids, adsorption on the surface, and flow, none of which are accounted for by equilibrium surface tension measurements alone. Thus, dynamic surface tension measurements are expected to be more relevant than equilibrium measurements to Marangoni-driven surface instabilities.

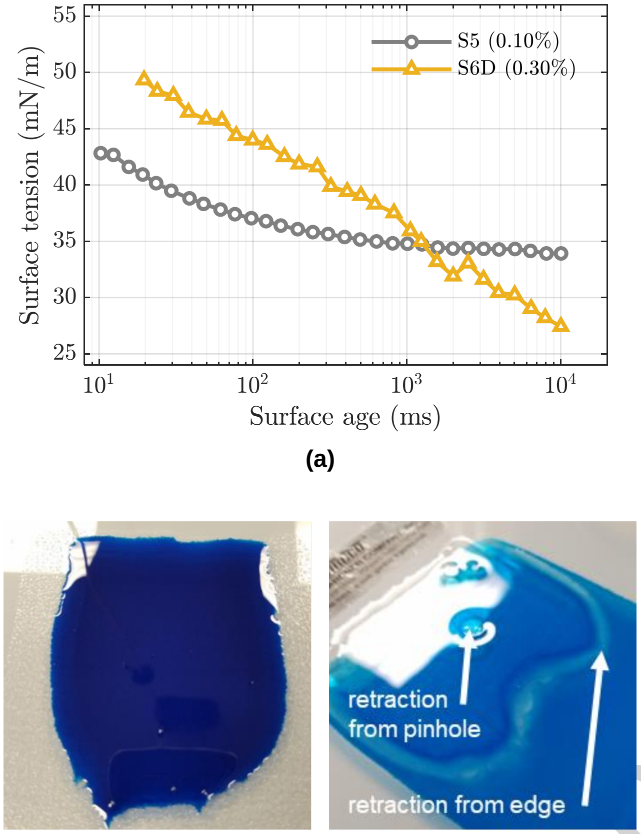
### *The role of dynamic surface tension in the Marangoni instability*

Dynamic surface tension (DST) is roughly a measure of the timescales of surface-active species's diffusion through the bulk and adsorption at the interface. It can be measured as a time-evolution of surface tension of a fluid pair following the creation of an interface between the two fluids, or as some value representative of a specific surface age. Equilibrium surface tension (EST) is then the value of the DST at infinite surface age. In practice, the dynamic surface tension of an aqueous solution can be measured by methods such as bubble tensiometry, which in our experiments could access time scales on the order of 10~10,000ms.

The apparent contradiction of the [equilibrium] surface tension grading rule in the work of Horiuchi, et al.[6] may thus be reconciled with the general Marangoni mechanism if the comparison of dynamic surface tensions showed that the surface tension grading rule is actually satisfied at some "short" (more relevant) timescale, despite being violated at longer time scales (at equilibrium or steady state). However, it is not known a priori how short of a timescale is relevant.

We probe this hypothesis with a model system comprising two aqeous solutions (no co-solvents) with different surfactants denoted S5 and S6D for shorthand. Figure 11 compares their DSTs: for short short timescales (early surface ages), the solution with S5 has a lower surface tension than that with S6D, whereas for longer timescales (at later surface ages; approaching equilibrium) the solution with S6D has the lower surface tension (i.e., lower EST). The DST crossover is on the order of 1000ms.

The model coating liquids in Figure 11b,c, are viscosified by addition of mthylcellulose (MC) loaded at 1% to bring the viscosities up to 1Pa·s, representative of our actual slurries. One of the liquids is colored by a blue dye for ease of visualization. Neither additive is appreciably surface active compared to the influence of the surfactants of interest. The DSTs cannot be measured directly for the coating liquids because of their high viscosity.



(a)

(b) (c)

**Figure 11. (a) Dynamic surface tensions of aqueous solutions with different surfactants S5 and S6D, measured by Kruss BP100 bubble pressure tensiometer at 22°C. (b) Coating of model liquid with surfactant S5 (blue) on top of model liquid with surfactant S6D (clear), with no surface instability. (c) Coating of model liquid with surfactant S6D (clear) on top of model liquid with surfactant S4 (blue), with surface instability manifesting as edge-in retraction (W-shaped ridge) and a growing pinhole.**

When the liquid with S5 was coated on top the liquid with S6D, the coated bilayer was stable (Figure 11b). Conversely when the liquid with S6D was coated on top of the liquid with S5, the coated bilayer exhibited surface instability of the top layer: the top layer appeared to retract edge-in and also from a pinhole (Figure 11c). That is, similarly to the examples of Horiuchi, et al.[6], the stable layer configuration appears to violate the surface tension rule by measuring the EST, but actually obeys it when measuring the DST at timescales < 1,000ms.

These observations and explanations are consistent with the observations of Valentini, et al.[7] who set out to study generally the capillary phenomena that affect multilayer and single layer slide coating of surfactant-laden aqeuous gelatin systems (for the photographic film industry). They observed that the ratio of DST (measured in the timescales of 100~1,000ms) between adjacent liquid pairs adequately explained the stability of the bilayer whereas the ratios of ESTs did not.

In summary, comparing the dynamic surface tensions at some arbitrarily short timescales of individual layers may be a good rule of thumb for ensuring compatibility of layer pairs in simultaneous multilayer coating for miscible systems, but not for the thermodynamic reasons that are most commonly described in the literature for immiscible layer pairs.

### *Elimination of surface instability in simultaneous multilayer coating*

Because our coating liquids are all-aqueous without co-solvents, we expect all layer pairs to be fully miscible and therefore without true interfaces. Attempted liquid-in-liquid pendant drop tensiometry experiments verify that interfacial tension between the aqueous supernatants is not measurable and that they appear miscible (Figure 12). The surfactant model system depicted in Figure 10 is closely related to our slurry formulations, and the results support the hypothesis that the Marangoni mechanism—not the thermodynamics of spreading—determines the surface instability during coating (Figure 8b).

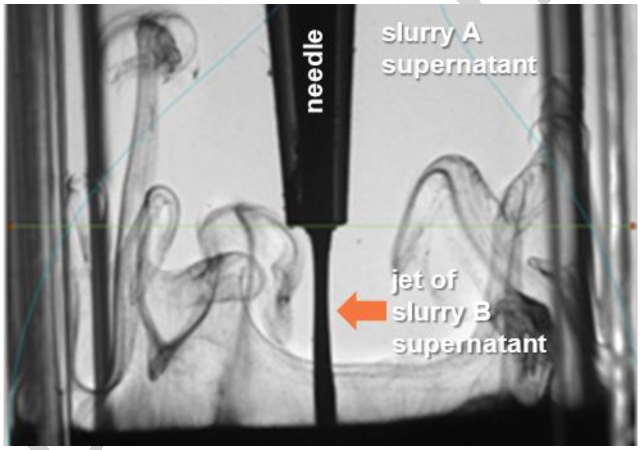


**Figure 12. Attempted pendant drop tensiometry of dark supernatant of slurry B (loaded with residual carbon black from the formulation) in the transparent supernatant of the slurry A, which is adjacent to it in our multilayer structure. The full slurry formulations could not be used because they are all opaque. Supernatant B cannot sustain a pendant drop within supernatant A, indicating lack of appreciable interfacial tension. The wispy clouds indicate supernatant B mixes into supernatant A. Both observations confirm that the all-aqueous formulations are mutually miscible.**

Table 2 organizes the equilibrium surface tensions (EST) of each incumbent slurry formulation (for single layer coating), together with a first reformulation and final reformulation (in which only the layer 6 slurry was reformulated). The first reformulation was based on the simplified premise that ratios of EST (which are easier to measure than DST) are a sufficient predictor for the Marangoni instability. The slurry viscosities were too high to measure EST by pendant drop tensiometry, so we used as proxies the ESTs of the supernatants of centrifuged slurries.

Table 2. Equilibrium surface tensions with air (EST) of incumbent and reformulated slurries' supernatants. Measured by Biolin Attension Theta tensiometer at 22°C.

| **Layer** | **EST (mN/m)** | | |
|---|---|---|---|
| | Before | First | Final |
| Layer 6 | 36 | 27 | 28 |
| Layer 5 | 28 | 30 | 30 |
| Layer 4 | 31 | 52 | 52 |
| Layer 3 | 53 | 54 | 54 |
| Layer 2 | 42 | 42 | 42 |
| Layer 1 | 40 | 64 | 64 |

Overall, the EST proved to be a reasonable indicator for layer compatibilities with respect to the Marangoni instability, with two exceptions. First, Layer 2 could not be reformulated to increase EST because of other constraints, but Layer 3 with a higher EST could nevertheless stably coat Layer 2. Second, Layers 5 and 6 were appropriately graded in EST after the first reformulation, but nevertheless the coating of the pair exhibited coating instability (Figure 8b).

Because Layers 2 and 3 were compatible, it was not practically necessary to further probe their DSTs. On the other hand, the incompatibility of Layers 5 and 6 suggested that the DSTs were improperly graded at some arbitrarily short time scale. Similarly to the EST measurements, the slurry viscosities were too high to reliably measure DST by bubble tensiometry, so we again used simple aqueous solutions loaded with similar amounts of the relevant surfactants as proxies to the slurries. Figure 13 compares the DSTs of these proxy surfactant solutions for Layers 5 and 6.

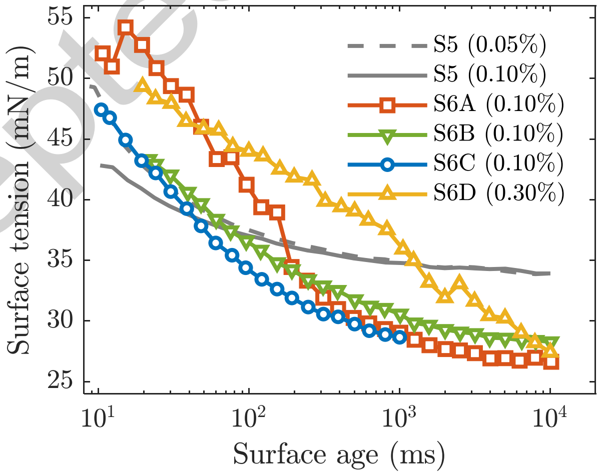


**Figure 13. Dynamic surface tensions (DST) of solutions with different surfactants. The DST curves for solutions S6A, S6B, S6C, and S6D cross over with that of S5 at different surface ages, indicating different "speeds" with which they can achieve lower DST than S5. All DST curves were measured by Kruss BP100 bubble pressure tensiometer at 22°C.**

The surfactant S5 is the one used in the Layer 5 slurry, which we fixed because it was deemed compatible with Layer 4 (it is also the same surfactant in the model system investigated in Figure 11). It is classified commercially as a “dynamic wetting agent” with comparatively high EST of ~34 mN/m. Doubling the loading from 0.05% to 0.10% does not appear to significantly change the EST or the DST curve. The surfactant S6A was chosen in the first reformulation of Layer 6 for its ability to depress the EST lower than that of S5. The surfactants S6B, S6C, and S6D were three candidates for further reformulation of Layer 6 after it was observed that S6A ultimately did not work (Figure 8b).

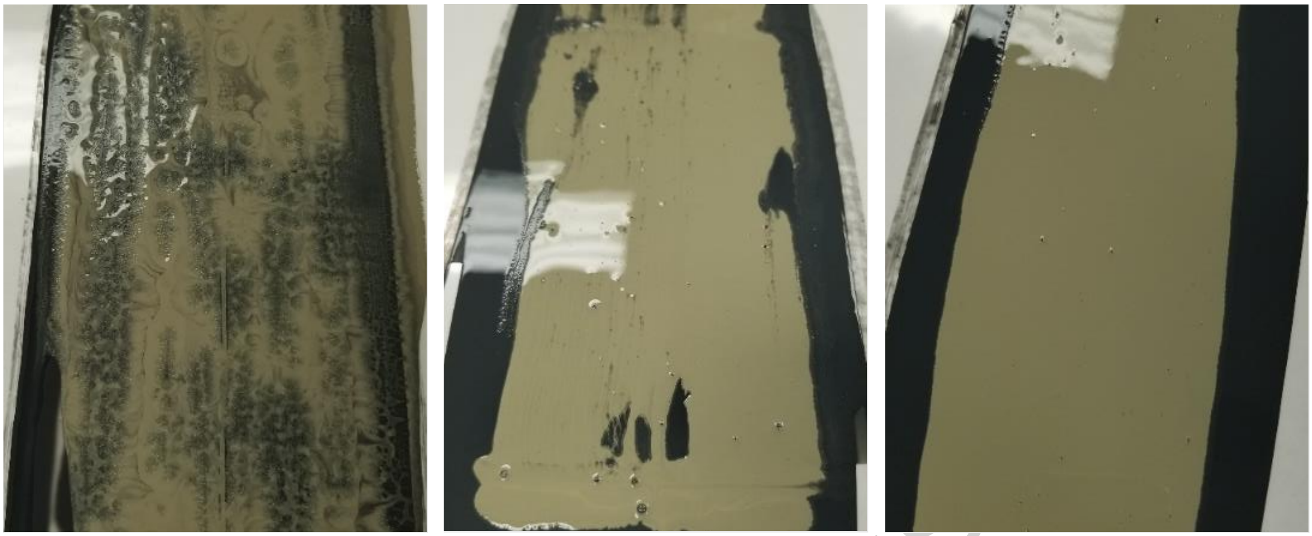
Figure 13 verifies that the pair S5 and S6A violates the surface tension grading rule for timescales shorter than about 200ms, but satisfies it for longer timescales. Similarly, the candidates S6B, S6C, and S6D all satisfy surface tension grading in the limit of EST but violate it at shorter timescales. The actual crossover timescale is different for each candidate. Their actual ESTs measured independently by pendant drop are summarized in Table 3 together with the values of DST at several surface ages.

Table 3. Comparison of EST and DST at different surface ages for different surfactants. Parentheses indicate difference from the value of S5.

| **Surfactant** | **Loading** | **DST @ 100ms** | **DST @ 200ms** | **EST** |
|---|---|---|---|---|
| S5 | 0.05% | 37 (+0) | 36 (+0) | 34 (+0) |
| S5 | 0.10% | 37 (+0) | 36 (+0) | 34 (+0) |
| S6A | 0.10% | 40 (+3) | 35 (−1) | 26 (−8) |
| S6B | 0.10% | 36 (−1) | 34 (−2) | 28 (−6) |
| S6C | 0.10% | 34 (−3) | 32 (−4) | 28 (−6) |
| S6D | 0.30% | 44 (+7) | 42 (+6) | 21 (−13) |

According to the hypothesis that DST ratios at some arbitrarily short timescale is a sufficient predictor for the multilayer coating instability, the candidate surfactants for Layer 6 can be rank ordered for their likelihood to solve the instability problem based on the crossover times of their DST curves. In this measure, S6D is least likely to work (as also suggested by the instability in the model system, Figure 11c), and less likely to work than the incumbent S6A.

Figure 14 compares hand drawdown coatings of the full slurries L5 and L6 formulated with the surfactants S6A, S6B, and S6C. Figure 14a verifies the slot coating outcome of Figure 8b. Both surfactant S6B and S6C seem to reduce the instability, with S6C appearing to be more effective than S6B (Figure 14b,c). Ultimately, we chose surfactant S6C in the final reformulation of the Layer 6 slurry, which resulted in acceptable coating quality in the multilayer slide coating.



(a) S6A (b) S6B (c) S6C

**Figure 14. Lab hand draw-down coatings of Layer 5 (black) with Layer 6 (green) formulated with different surfactants as labeled; detailed comparison to S5 in Figure 8 and Table 3.**

### *Discussion on DST grading and mechanisms of multilayer coating instability*

The agreement between the rank-ordering of coating quality (Figure 14) and the rank-ordering of DST crossover time lends credence to the general idea that comparing DST crossover times can indicate multilayer instability. It is tempting to assign some significance to the timescale of 50~100ms, which seems to discriminate well the compatibility of Layer 6 surfactants with Layer 5. However, any quantitative comparisons must account for the complicated and coupled dynamics of diffusion, adsorption, and flow.

Valentini, et al.[7] found that DST ratios measured at timescales in the range of 10~1,000ms were adequate to predict multilayer instability, but noted that the range of timescales did not align with the range of timescales corresponding to the coating process dynamics. The disparity between timescales is even more salient in our example in which we measure the DST on proxy liquids rather than the full coating formulations.

This lack of a quantitative link between the dynamic surface tension (DST) and the Marangoni phenomenon hinders our ability to properly predict the Marangoni instability. Nevertheless, our observations together with the literature suggest that the dynamic surface tension rule may at least substantially facilitate recipe development by decreasing the amount of slot coating experiments whenever a layer pair comprises different types of surfactants: surfactants and concentrations may be screened by comparing the DST cross-overs relative to recipes that exhibit instability. By these arguments, grading the equilibrium surface tensions may be sufficient for simpler formulations with the same surfactant shared across the layers when the surface tensions directly indicate the potential for surface-tension-depression in the top layer to the thermodynamic driving force of diffusion.

In summary, this instability in miscible multilayer systems is driven by concentration gradients of surface active species. In all cases, and regardless of what can practically be measured, minimizing those gradients or structuring them advantageously (i.e., with the concentration gradient moving downwards from the top layer) presents the formulator with the best case system for stable multilayer coating. Alternatively, because this mechanism is kinetically rather than thermodynamically-driven, slowing diffusion timescales by increasing layer thicknesses and viscosities is another available strategy for improving stability [6].

Finally, we note that the Marangoni phenomenon and spreading between immiscible layers is not mutually exclusive: it is possible that a species soluble/miscible in two adjacent immiscible films may alter the interface between the layers and/or alter the surface of the top layer to induce a Marangoni instability despite the individual layers obeying the surface tension grading rule.

## Summary

Simultaneous multilayer coating is an attractive method for efficiently fabricating multilayered structures, whose demand may increase in the coming years for applications such as fuel cells, batteries, capacitors, etc. Yet the publicly available knowhow around multilayer coating has not expanded much beyond the traditional applications.

We have reported on two issues in simultaneous multilayer coating related to the slurry nature of our coating liquids: particle jamming in the die internals associated with shear thickening of high particle loadings, and a surface instability (resembling top layer de-wetting) associated with the presence of different wetting agents and dispersants in different amounts in each layer.

Particle jamming and associated coatability issues may be linked with shear thickening. We have shown that these issues may be eliminated by adding low concentrations of viscosifiers (reactive thickener). Although the effect is not unprecedented, the exact mechanisms appear to be unknown in the literature. Further systematic work in this area could provide better guidance for formulation of highly loaded slurries, which are sure to become more relevant in applications such as batteries and fuel cells.

For fully miscible liquids with no true interface between them, the surface instability resembling de-wetting is likely a surface tension gradient (Marangoni) driven rupturing film flow in the top surface. The surface tension gradients are set up by species such as surfactants and co-solvents that diffuse from buried layers into the exposed top surface and locally depress the surface tension with the surrounding air.

According to the literature [7] and our own experiments, the comparison of dynamic surface tensions of individual layers is relevant to predicting the bilayer instability: surface tension differences measured at arbitrarily short timescales qualitatively indicates the potential for species to diffuse into the top layer and depress its surface tension. The dynamic surface tension grading rule is thus a useful one in practice, as long as its motivations and limitations are clear. For immiscible multilayer systems, it is a simplified version of spreading coefficient arguments and interfacial tensions between the adjacent liquid layers must be considered when they are not neglible. For miscible multilayer systems, the rule is only an indirect prediction of the potential for Marangoni flows to develop and cannot be used directly to predict stability: violating the dynamic surface tension grading at arbitrarily short timescales does not necessarily lead to instability, nor does satisfying the rule at all measurable timescales ensure stability.

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