# Internal Stress: Part I

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## Cumulative Stress versus Adhesive and Cohesive Strength

To this point, our discussion of the mechanics of paint film failure has considered only the positive forces of cohesion and adhesion, which hold the film together and to the substrate. As noted in the October 1995 JPCL, a complex system of opposing forces acts against film cohesion (tensile strength) and adhesion. When these forces are large enough compared to the cohesive and adhesive strengths of the film, they can produce either cohesive or adhesive failure in the coating system. Statements to the effect that adhesion is poor tell only part of the story. This statement really means that the adhesive strength is not sufficient to maintain adhesion under the stress conditions that act upon the film. If the magnitude of the stress is reduced, then that same adhesive strength may be quite adequate to sustain system integrity.

## Review of Tensile and Compressive Stresses

The forces or stresses that oppose adhesion and cohesion are diverse. They depend on the service conditions under which the film operates; the film's chemistry, composition, curing mechanisms, thickness, and age; and the conditions under which film formation took place. These stresses can be internal (e.g., film formation, thermal history, pigmentation effects, aging effects, film thickness effects); external (e.g., bending and forming, abrasion and impact, solvent absorption, electrical stress, chemical attack, substrate effects); and hygrothermal (e.g., thermal effects, hygroscopic effects).

In general, stresses may be either tensile or compressive. Both may be counterproductive to the adhesion and cohesion of the film. Tensile stresses result when the coating contracts. Typical tensile stresses occur from film formation or exposure of the film to cold. Compressive stresses result from expansion of the film and are incurred as the film responds to high humidity or elevated
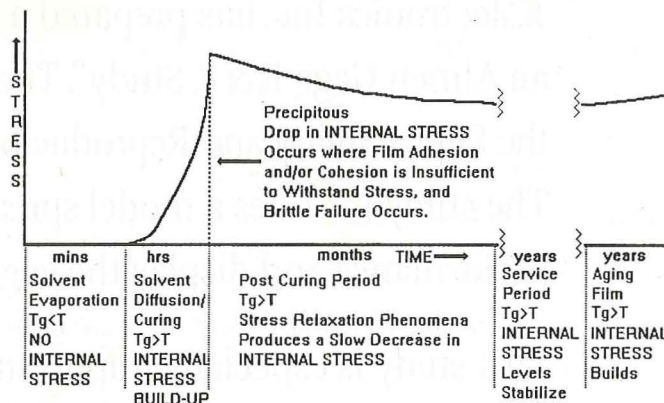


Fig. 1. Internal stress and the life cycle of the coating film

temperatures. Because the latter stresses result from changes that tend to increase $T-T_g$, reducing modulus and flexibilizing the film, they are more likely to be dissipated than tensile stresses. Compressive stresses, therefore, are less damaging than tensile stresses. There are many exceptions to this rule, however, because large compressive stresses resulting in gross film deformation can be very destructive. These large compressive stresses are utilized, for example, in removing films from substrates with paint removers.

## Cumulative Nature of Stresses

While the convention is entirely arbitrary, some authorities[1] assign a positive sign to tensile stresses and a negative sign to compressive stresses. This is convenient, for while both tensile and compressive stresses independently act against adhesion (and cohesion), the total stress on a coating system is cumulative. Tensile and compressive stresses derived from different sources and applied simultaneously may compensate for one another, thus reducing the cumulative stress levels. As an example, exposure of the paint system to hot solvent results in a total compounded stress ($S_{TOT}$) that is derived from compressive components relating to film expansion from increased temperature ($S_T$) and to absorption of the solvent ($S_H$) and consequent free volume increase, i.e., $S_{TOT} = -(S_H + S_T)$.

In this case, both the absorption stress, $S_H$, and the thermally induced stress, $S_T$, are additive. Together, they will produce more opposition to adhesion (and cohesion) than will a condition where the solvated film is subsequently dried using a hot air drier. In the latter example, the diverse stresses are subtractive; while the film is desorbing solvent, it shrinks in volume, and tensile stresses are induced in the film as the free volume is reduced. Simultaneously, however, the film is also under the influence of the hot air drier, which creates compressive stresses due to the expansion of the film by heat. One stress counteracts the other, and the cumulative stresses against adhesion and cohesion are reduced, i.e., $S_{TOT} = S_H - S_T$.

## Internal and External Stress

The service or external stresses that affect a paint system are readily anticipated. Stress from external sources, including impact, flexing, vibrations, and abrasions, are obvious. The hygrothermal stresses that result from the paint film and substrate's response to environmentally induced thermal and humidity gradients are also generally well understood. Less appreciated are the internal stresses derived from the paint film as it adjusts from the wet film to the dry film and then more slowly to those gradual molecular changes that accompany (or more accurately, produce) the aging process. These stresses are almost always tensile in nature, especially those that originate during film formation and cure.

These stresses make up a substantial, if not the paramount, component of the total stress accretion. They are often not taken into account by those who use, specify, or formulate coating systems.

## The Effect of Internal Stress

Some degree of internal stress exists within all coating films.[2] It is always counterproductive to good mechanical properties and, consequently, to performance. Only where high compressive stresses (from the environment or service condition) act upon the coating would a tensile internal stress promote adhesion and cohesion because of its counterbalancing effect on the overall stress condition. In most cases, however, the forces of internal stress are smaller than the cohesive and adhesive forces that maintain the integrity of the film. In most cases, therefore, internal stress is simply stored within the film and thus reduces the system's ability to accommodate additional tensile stresses from external hygrothermal sources during service.[3,4]

In extreme cases, internal stress alone may be sufficient to promote spontaneous peeling (where the internal stress is larger than the adhesive strength of the film) or cracking (where the internal stress exceeds the film's cohesive strength[4,5]). While extreme, these cases are by no means rare.

Internal stress can be very large. An epoxy film, applied and cured on aluminum foil, curls up as cure advances and the film shrinks. Internal stresses build up on curing, readily deforming the thin foil. This deformation allows a degree of stress dissipation. But what happens when the aluminum substrate is thicker and much stronger, or when an even stronger steel substrate is substi-

tuted? The internal stress developed within the coating remains the same, but now the stress cannot be dissipated in any deformation of the "too strong" substrate. Instead, it must build up as an internal strain within the system. The only way such strain may be relieved is by some deformation of the coating film (reversible or irreversible) or by brittle failure (i.e., cracking of the film or its release from the substrate).

The nature of the response is dictated by the mechanical property profile of the coating film. (See Trouble with Paint, JPCL, March 1996.) Hard, fragile films with low elongation properties and poor tensile strength undergo brittle failure and crack. If stress is high enough and adhesion is poor enough, hard films with high tensile strength but equally low elongation are more likely to delaminate, a second manifestation of brittle failure. Soft films of high elongation and low tensile strength will stretch reversibly, while soft, weak films with lower elongation will undergo irreversible deformation. Finally, tough, elastic films (i.e., films with high tensile strength and high elongation at break and yield values) will best resist both brittle failure and irreversible deformation. In the latter case, where adhesive and cohesive strengths are too strong for any mechanical failure under the stress levels incurred, the stress will be locked into the coating as a strain. Stress levels may dissipate very slowly over time (stress relaxation), but while they remain, they will inevitably reduce the amount of additional stress that the film will tolerate without failure. For example, the impact of a stone produces failure (chipping) of a film under high internal stress, whereas the same impact may produce little or no failure on a film under low internal stress.

## The Causes of Internal Stress
### General Origins of Internal Stress

Internal stresses originate during the film formation and curing processes as a result of solvent evaporation in all films and the cross-linking of thermosetting films.[2,6] Both processes produce a volumetric compaction or shrinkage of the film. In adherent paint films, this shrinkage occurs with some resistance, if only from the adhesion of the film to the substrate. This resistance is a source of internal stress. In most films, however, shrinkage is also hindered by other equally restrictive factors. An example is restriction at the molecular level involving steric hindrances incurred by configurational and conformational "obstructions" (e.g., interchain cross-links, bulky side groups, hydrogen bonds, and chain entanglements). Whatever the cause, these restrictions of the natural film compaction are the major source of internal stress.

In most coating systems (some, such as oxidizing films, more than others), internal stress is also produced by the paint film's aging processes (Fig. 1). This stress is a result of long-term, environmentally induced changes in molecular morphology and structure. The gradual accumulation of resultant stress within the coatings plays a large part in the deterioration of the mechanical properties of the aging film. Generally, the deterioration is characterized by increased modulus and reduced elongation at break.

### Free Volume and Solvent Loss

We have already shown in our discussion of free volume

(Trouble with Paint, <u>JPCL</u>, January 1996) that during film formation, as solvents leave the film, they create molecular "holes" or free volume spaces into which the molecular segments of binder should ideally migrate. This process results in an overall compaction of film volume that is proportional to the amount of solvent lost. Film compaction or shrinkage can occur without much difficulty during the early evaporational (volatility-controlled) stage of drying. In this stage, the film is still low in viscosity, and the binder molecules are very mobile (i.e., free volume of the film is high, and the $T_g$ is lower than the film temperature). With progressive lost of solvent, however, the binder molecules approach each other more closely, and volatility-controlled solvent loss mechanisms give way to diffusion-controlled processes.

### Internal Stress from Solvent Evaporation

In thermoplastics, semi-permanent secondary valency bonds begin to be set up, while in thermosetting systems, more permanent primary bonds (cross-links) are formed between neighboring chains. Some secondary valency bonding may also occur in areas of a thermosetting matrix. These bondings and cross-links in one segment of the polymer may severely restrict the ability of the adjacent polymer segments to migrate into the holes left by the vacating solvent molecules. This occurs particularly in coiled or branch-chained segments. Such bondings and cross-links not only restrict polymeric mobility in this way, but also prop the structure apart, locking in a degree of free volume and locally preventing further potential volumetric shrinkage. A similar phenomenon may arise from bulky side groups and branches that effectively impede interchain associations in adjacent segments (Fig. 2).

All of these restrictions add up to a primary source of internal stress, as the increasing $T_g$ of the forming film reaches and exceeds the film temperature.[7] Under these conditions, the opportunity for stress release through conformational adjustment of the polymer (by segmental rotation, for example) is greatly diminished.

### Internal Stress from Polymerization

In thermosetting (chemically curing) systems, two separate phenomena are involved: solvent release (as discussed above) and polymerization.[2,6,8] Here, things are a little more complex. Polymerization also produces volumetric contraction of the curing film.[9] Because covalent bonds are formed during polymerization, the final reacted bond lengths are shorter than the pre-reaction distances of the reacting molecules (Fig. 3). Thus, the polymerization reaction pulls the entire polymeric matrix together, resulting in an overall shrinkage in volume. Where this volumetric shrinkage is impeded by bonds already formed, stress inevitably results. Where solvent evaporation can entirely precede the subsequent polymerization and the polymer is liquid, the solvent-free film may still be low enough in viscosity before substantial polymerization occurs. This allows more efficient depletion of free volume before the $T_g$ builds beyond the temperature of the film (i.e., before solidification). In this case, the reacting molecules have the opportunity to settle into a relatively compact conformation before the cross-linking reaction occurs. The consequent film will inevitably have
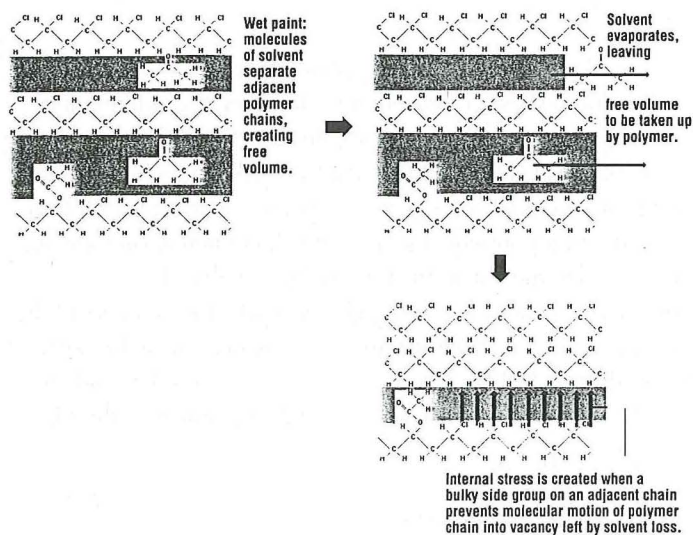


Fig.2. *Formation of internal stress during drying of film.*

lower internal stress than where film formation (solidification) takes place before the solvent has left the film. Under the latter circumstances, free volume is locked within the film and more substantially impedes the natural reduction in volume (shrinkage).

### Effect of Solvent Evaporation Rate on Internal Stress

In the thermosetting polymers, internal stress levels will therefore be dictated by the relative rates of solvent loss and polymerization. Working with epoxy systems, Shimbo et al. conclude[10] that internal stresses are virtually absent while the film remains in the rubbery region and only occur in the glassy region. Working with epoxy films, Croll has studied the stress of epoxies formulated with slow solvents that are released from the film only after the cross-linked structure begins to be set up. These films incur increased stress (or strain) as film thicknesses increase because solvent diffusion continues after solidification.[8] The thicker the film, the more solvent retained in the curing film so that substantial solvent has to leave the film after solidification. This process leads to greater residual stress.

Similar systems based on faster solvents, substantially released from the film before solidification, show less increase in internal stress with increasing film thickness. Croll concludes that if the use of very slow solvents in such thermosets is unavoidable, then successive coats of thin films should be applied at recoat intervals long enough to ensure cross-linking of each coat before the application of the next.[8] This approach is preferable from the standpoints of strain reduction and optimum adhesion. In non-cross-linking systems, conversely, slower solvents have been noted to produce less internal stress than faster evaporating ones. In the latter case, the slow solvents are thought to act as plasticizers and facilitate stress relaxation in the latter stages of drying.[1]

In latex systems also, appropriate selection of coalescents and adjustments of their concentration are important to the minimization and rate of internal stress build-up. The effects are related to plasticization and the rates of diffusion of the coalescents from the film.
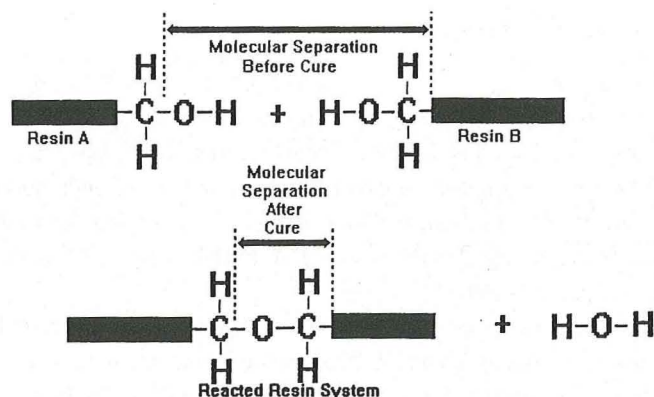
*Fig. 3. Shrinkage on polymerization as a source of internal stress*

## Wrinkling Phenomena

Oil paints and long oil alkyds cure through relatively slow oxidative processes that allow complete solvent release before final polymerization. These coatings are less prone to high residual internal stress (at least during film formation) than are many other thermosets that cross-link more rapidly. In excessively thick films, however, internal stresses can occur because the lower layers of the film cure more slowly than the upper layers, which have more access to oxygen. Subsequent curing of the lower layers and their associated shrinkage set up internal strains that contract the already cured top skin of the film. The surface then wrinkles or shrivels in the typical pattern of many alternating ridges and valleys. In this manner, the surface of the film accommodates the delayed shrinkage of the lower layers.

Once very common with unmodified oil paints and very long oil alkyd systems, the problem has reemerged since the introduction of alkyds with low levels of volatile organic compounds (VOC). These newer, rather monodisperse (see Trouble with Paint, JPCL, November 1995) resins of lower molecular weight and higher fatty acid content surface-dry more rapidly, but they are slower to through-dry in the absence of lead driers. Slow drying encourages wrinkling. Applying these systems at higher rather than lower film thickness (because of the higher solids content) further exacerbates the difficulties. Pigmentation with barrier pigments, which further excludes oxygen access to the lower layers of the film, is, in all cases, counterproductive to relief of wrinkling.

Coatings with high pigment volume concentration (PVC) are more porous and so allow higher oxygen transmission rates. These higher rates and the reduced cohesion of their surface layers both minimize wrinkling.

In some films, wrinkling may be so fine that is looks like blushing or loss of gloss. In others, patterns are clearly visible. The severity of the problem as well the amplitude of the wrinkle is increased with increasing film thickness.

Wrinkling is also found in ultraviolet light-cured acrylics pigmented with strongly ultraviolet light-absorbent pigments. In this case, it is caused by a similar heterogeneous cross-linking of surface and under-layers.[11] Cross-linking at the surface is rapid because the surface layers have greater access to ultraviolet light radiation. In deeper layers of the film, the ultraviolet light is preferentially absorbed by the pigment; therefore, these deeper layers are slower to cure.

Some relief is possible by increasing or changing the photoinitiator or by increasing the levels of oxygen above the surface of the film. Increased levels of oxygen inhibit surface cure and therefore the differences between the cure of the surface and the deeper layers are reduced, slowing cure universally. This latter remedy is not appropriate for cationic ultraviolet light-curing systems, for these systems are not oxygen inhibited. Here, the best remedies seem to be to avoid using highly ultraviolet light-absorbent pigments or to control film thicknesses to very low levels.

Wrinkling may also be encountered in baking systems cross-linked with formaldehyde resin and catalyzed by amine-blocked paratoluene sulfonic acid. In this case, heterogeneous cure is caused by the greater availability of free acid at the surface of the film (allowing surface cure). Within the system, curing is reduced because of the amine block. Amine volatility and the strength of the association between the amine and the acid appear critical. Triethylamine is a particularly bad offender.

Again, increasing film thickness is counterproductive to resolution of the problem. The phenomenon is described by Wicks and Chen using water-soluble melamine formaldehyde cross-linked acrylics.[12]

## Internal Stress in Other Systems

In other systems (polyurethanes and nitrocellulose lacquers), increasing film thickness is also seen to produce very high levels of stress.[2] These relationships are greatly complicated by the solvent systems used and by the curing agent types, where applicable. In thermoplastics, high levels of plasticizer reduce $T_g$ and allow greater polymeric mobility, thereby relieving stress. In some respects, the plasticizers may be considered non-volatile solvents. Being molecularly smaller than the long chain polymeric molecules, the plasticizers are less encumbered by chain entanglements and molecular associations. Plasticizers are therefore freer to migrate into the free volume spaces left by the lost solvent. Thus, the plasticized film is generally less susceptible to the build-up of internal strain than the non-plasticized film.

Compared to alkyds of similar oil length cured oxidatively, aminomodified short oil films have poor adhesion. This is related to the higher levels of internal stress produced by the creation and subsequent loss of solvent and other condensing moieties (water, formaldehyde) from the curing reactions and the entrapped free volume resulting after the cross-linked structure of the baked film begins to be established. Fortunately, the effect is offset somewhat by the higher temperatures (temperatures above the $T_g$) at which the reaction proceeds and molecular mobility is maintained.

These internal stress effects of the condensation reactons are not seen with ring-opening epoxy polymerization (with amines and acids). In these reactions, there is no lost condensation product, and less shrinkage as molecules combine. Thus, epoxy/amines and epoxy/polyamides have much better adhesion than the amino/formaldehyde systems and even epoxy/phenolics.

Bingo No. 6

# Points to Ponder

- How did a fool and his money GET together?

- If nothing sticks to Teflon, how do they stick Teflon on the pan?

- Why is abbreviation such a long word?

- If you shoot a mime, should you use a silencer?

- Is it true that cannibals don't eat clowns because they taste funny?

- Why do they call it a TV set when you only get one?

- How do they get a deer to cross at that yellow road sign?

- Why is there an expiration date on the sour cream container?

- What's another word for thesaurus?

**Conclusion**

Internal stress has much bearing on the behavior, aging process, and failure mechanics of coating films. Today, especially when we use so many strong thermosetting systems of high modulus and $T_g$, the significance of internal stress to paint film behavior may be as important as the ratio of PVC to critical pigment volume concentration (CPVC).

Our discussion will continue in the next column (reprinted in the next issue of *Aircraft Paint Stripping News*), when we will examine the origins of internal stress, other than from the film formation process, and consider the effects of pigmentation and film thickness on the phenomenon. Finally, we will consider the dissipation of internal stress.

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