

Mechanically-Induced Stress from the Manufacturing Process

by Clive H. Hare
Coating System Design, Inc.

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The imposition of externally derived mechanical stress on paint films is a major factor in paint film performance. Stress manifestations, ranging from deformation (flexing, stamping, impact, and bending) to wear (abrasion, scuffing, burnishing, scratching, chipping and grinding), are numerous. In practice, these stresses may be quite specific, but their sources are very diverse.

The paint system responds to mechanically-induced stresses predominantly by physical change. The nature and magnitude of the physical change may also vary, depending upon the temperature and rate of applied stress, as well as other conditions under which the stress is applied (the presence of water and chemicals, for example). Chemical degradation in polymers can result from mechanical stress (such as the depolymerization of natural rubber by grinding and kneading in the presence of oxygen), but physical changes induced by such stresses are immediately more obvious and generally precede chemical degradation of the film.

The effects of external mechanical stresses on coating films are more readily understood than those of internal stress and other more subtle stress phenomena. This statement is particularly true for physical stresses related to the service environment (the chipping of a car finish under the impact of road gravel, for example). It also applies, if to a lesser degree, where stresses are derived from the manufacturing process (post forming, drawing or stamping of pre-coated metal). However, the scientific categorization and meaningful quantification of many stress phenomena, particularly service stress phenomena, remain elusive. The present article describes weaknesses in current testing protocols, a variety of manufacturing stresses, the effects of the substrate and the film on manufacturing stresses, deformation of a coating, and tests for deformability.

Current Testing and Analysis

There is a lack of adequate laboratory testing protocols to accurately simulate (and ideally accelerate) what goes on in the field. Many of the standard tests used by the industry to "measure" the physical property profiles of coating films often do not represent the physical conditions existing in practice or are not appropriately applied. What does Taber abrasion tell us of the wear on structural steel bridge coatings? What value are cylindrical mandrel determinations derived in the laboratory at 25C (77F) on a 10C (50F) glass transition (T_g) coating, when the coating is flexed in service at or below freezing?

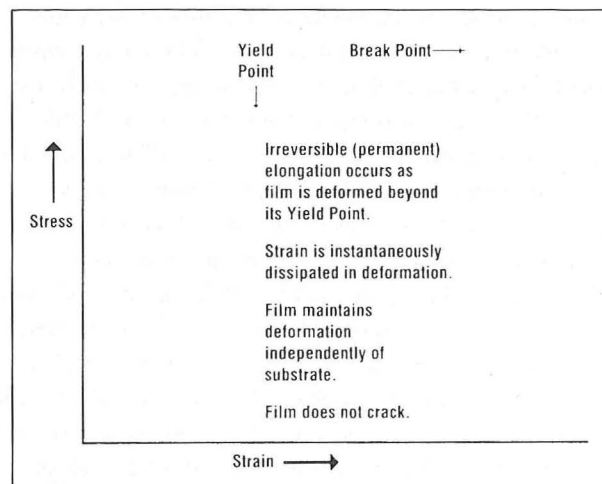


Fig. 1a. Response of adherent coil coating to deformation: irreversible flow in deformable system. (Figures courtesy of the author.)

Only in the last 20 years have more universal and scientific techniques such as stress/strain analysis and dynamic mechanical analysis been applied to quantify the mechanical properties of coatings. From this vantage, there is still a long way to go before the empirical approach, widely used by the coatings industry, is either replaced or amalgamated into the more fundamental analysis that is used in the rubber and plastics industry. In defense of our own industry, it may be argued that there are complications in coating film behavior not encountered in these other industries. Not the least of these complications are the presence of the substrate, the lamella heterogeneity of superimposed films of practical coating systems, and the comparatively meager cross-sections involved. Variations in film structure relating to cross-link density, film thickness, solvent retention, and the distribution of pigmentation (especially platy and acicular pigmentation) also affect coating film behavior under stress and complicate adequate categorization.

Manufacturing (Deformation) Stresses

Manufacturing stresses are incurred in coating films from post-painting processes that involve bending, stamping, forming, drawing, or otherwise deforming an already coated substrate (usually a metal). Ideally, this deformation should be accomplished without producing cracking, delamination, or any other fatal flaw in the substrate and coating system. Among items so manufactured are architectural and residential sidings, guttering, appliance cabinets, automobile body parts and accessories, window blinds, cans, fluorescent lighting fixtures and bottle tops.

In each case, the applied film must deform without failure as the coated sheet is shaped at the temperature and rate at which

the forming stress is applied. That is, the film must be capable of undergoing the necessary (preferably irreversible) deformation without exceeding its elongation at break. The ideal coating should exhibit stress/strain behavior typical of that depicted in Fig. 1a. Elastic behavior Fig. 1b, is less ideal, the strain developed in the coatings as the metal is deformed will be retained, and the applied coating system will be less capable of withstanding any additional post-forming stresses than would have been the case were the strain to have been dissipated in irreversible deformation. Elastic behavior of the type depicted in Fig. 1c is unsatisfactory because the coating fails during forming. As noted many times in this series, the exact shape of the stress/strain curve will be markedly affected by the temperature and rate of the forming process. Changes in either can so foreshorten the elongation at break that brittle failure, such as cracking or delamination, may occur.

Most coatings have property profiles that are compromises between two or more necessary but conflicting attributes. Thus, most coatings may be quite sensitive to changes in very specific forming rates and temperatures. An example is can coatings which are applied to blanks before fabricating draw and redraw two piece cans, for example. These coatings must not only be capable of withstanding the drawing process, but must also be able to resist chemical degradation by the can's contents. The coatings must also form a barrier strong enough between the contents and the metal so the substrate does not alter the flavor of the contents. Even cans that are coated after fabrication must be crimped as they are sealed by the packer, so the coated substrates must have enough flexibility to withstand the stresses of this application. Chemical resistance properties are maximized with increasing Tg and cross-link density. The formulator of can coatings must emphasize these properties as far as possible without jeopardizing the formability that is favored by decreasing Tg. If, however, even a well balanced composition is drawn too rapidly or at too low a temperature, then the mechanical properties may be insufficient to avoid brittle failure (cracking and or delamination).

Similarly, the design and cure of coil coatings for high performance architectural siding must be optimized carefully. These coatings are intended to achieve long-term (20 year) durability and weathering resistance, while still retaining enough flexibility to withstand the extension necessary during post-coating forming operations without cracking. In winter, cold, precoated stock (perhaps stored in unheated warehouses) is likely to be fabricated at a lower temperature than would be the case in summer. Unless the coating is designed for such low temperature forming, it may crack. It is, therefore, important that lower threshold temperatures for forming be well defined by the manufacturer.

When the chemical resistance or hardness requirements of the end use are such that low temperature fabrication is not possible without failure, then changes must be made. Storage temperatures must be raised, the rates of deformation must be reduced, or the formulation must be adjusted.

The cost advantages of the coil coating process depend on the maintenance of good line speeds in coating and post-forming operations. The coating line must run at very high speeds (400 ft min) with dwell times in baking ovens of 15 to 45 seconds at 250C

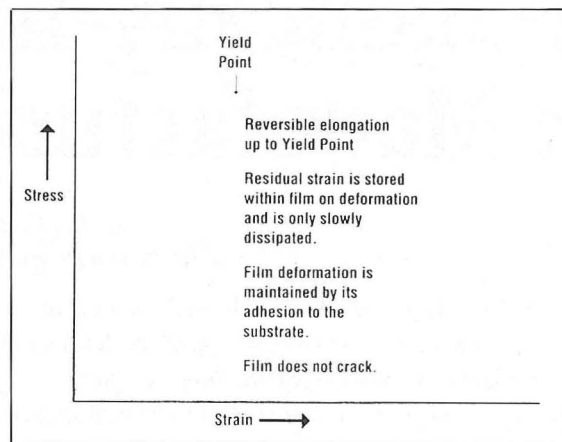


Fig. 1b

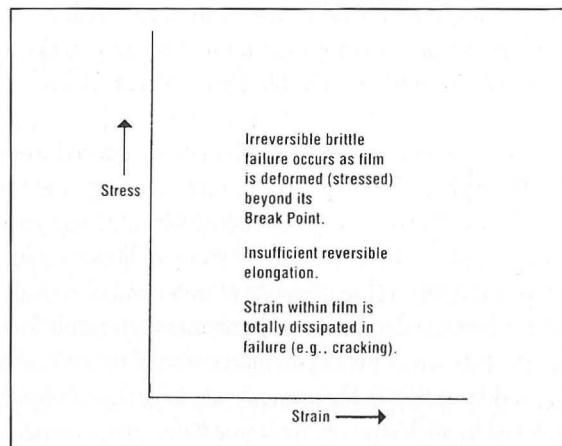


Fig. 1c

Fig. 1b. Response of adherent coil coating to deformation: Reversible deformation in elastic film

Fig. 1c. Response of adherent coil coating to deformation: Failure in rigid system

(482F). With fluoropolymers, still higher temperature cures are required. Variations in these temperatures can cause problems in both color control and cure (and, therefore, in the mechanical properties of the coating). After coating, the coils are rewound. The coated film must be hard enough to withstand the high internal pressures within the tightly wound coils without blocking or pressure mottling. Storage temperatures, which may reach 90C (194F) in summer, may cause problems if the Tg of the coating is too low. When the coating coils are subsequently unwound and the stock cut and stacked, the stacks may weigh several tons, which also puts demands on the non-blocking properties. Handling operations, rolling and dragging (during forming and erection as well as manufacturing) will also mar the coated material. (To minimize marring, small quantities of high melting point polyethylene waxes are incorporated in the finish formulation. These additives are also in the backing coatings.) Finally, the coated steel must be shaped in the forming operation. It is indispensable that these operation be performed so that cracking does not occur

along the convexity and bend of the fabricated part. Again, changes in either rate (increasing) or temperature (decreasing) of the forming operation may have the same effect as raising the film modulus. These changes may in turn foreshorten the elongation at break properties so that it may be difficult to avoid cracking on forming.

In practice, cracking often occurs along the bends of coil-coated sidings. Such cracks are less prevalent with the high end, high performance coatings, such as the thermoplastic fluoropolymers, than they are with some of the alkyds, acrylics, and polyester-based systems. Where aluminum and galvanized substrates are coated with high performance coating systems (usually primed with chromate-pigmented epoxies), the cracks, which may extend into the metal itself, may remain innocuous. The bases of the V-shaped cracks along the convexities of the bend are quickly sealed with a polarizing film of corrosion product. In cheaper alkyd-coated stock for less demanding applications, cracking itself is not so much the problem as is the subsequent corrosive breakdown that may propagate from the cracked line.

The attack may be intensified in stacked bundles of cut sheets when water becomes entrapped between the sheets, and crevice corrosion may occur. Crevice corrosion may result from condensation produced from the shipment of either cold coiled or cut stock into warm, humid areas. It can be particularly virulent where the cut stock bundles are subject to salt water from their transport over salt-laden roads in winter, or from unfavorable storage conditions. Storage is most advantageously arranged using spacers between sheets and angle stacks to facilitate adequate drainage of water from between the adjacent panels. The stacks must also be covered to prevent their rewetting.

A similar problem of salt-induced corrosion occurred on a white coil coating during the embossing of a decorative aluminum wall panel. Microcracking resulting from brittle failure led to severe corrosive deterioration of the panels in subsequent service in a meat packing plant. The failure was manifested as undercuts radiating from the exposed metal at the base of the crack. Here, the primary electrolytes that accelerated the aluminum corrosion were strongly alkaline cleaning agents and hypochlorite solutions, which attacked the panels at the exposed aluminum sites. On non-embossed panels where the coating was not cracked, there was no failure.

Effects of Substrate, Adhesion, and Thickness

The presence of the substrate, the film interaction with the substrate, and the thickness of both substrate and the film greatly affect the deformation properties of applied coating films. As Wicks, et al.¹ point out, the substrate can markedly reduce the unfavorable effects of deformation on the coating. Improved adhesion, resulting from increased interaction between paint film and substrate, inevitably increases the amount of stress that is necessary to produce brittle failures in these systems. This result may occur because stress is in part transferred to the metal, instead of being stored within the coating. The substrate is in this case acting as an energy sink.

It is well appreciated by any technician familiar with empirical testing methodology for flexibility (ASTM D522) and impact (ASTM D 2794) that both the thickness of the metal and that of the film have great impact on the ability of the film to resist deformation. Schuh and Theuerer² have shown that percent elongation (E) is related to the thickness of the metal (t) as well as to the radius of the mandrel (r) as $E=100t/(2r+t)$. Fig. 2 shows the relationship of the mandrel diameter to the extent of the elongation to which the coated coupon may be exposed during the bend test: the smaller the mandrel diameter, the higher the elongation and the more severe the effect on the coating. Fig. 3 illustrates the fact that the elongation also increases as the thickness of the coating being bent increases; thus, thicker films must endure higher stress than thinner films, and are therefore more prone to crack when bent over an identical mandrel. A similar effect is also noted as the thickness of the substrate increases (Fig. 4), for here too, percentage elongation increases as identical films of the same film thickness are applied to progressively thicker panels and bent over the same mandrel.

Compared to thicker films, thin films will withstand far greater deformation, more rapid deformation, and deformation at lower temperatures. It is for this reason that coil coating systems are so much lower in film thickness than maintenance coatings. Interior can coatings may be as low as 0.1 mils (2.5 micrometers) while coating systems for coil stock designed for appliance cabinets are normally about 1 mil (25 micrometers). If a coil coating of a greater thickness cracks or delaminates when deformed, it may still be used if its film thickness can be reduced sufficiently without unduly affecting either corrosion resistance or opacity.

In the 1970's and 1980's, coil coated stock for automobile body parts was coated with a proprietary, specialized zinc-rich, chromate-complexed, two coat, single component, linear epoxy based system for added corrosion resistance. Along with the ability to be welded and overcoated, one of the primary properties demanded of this system was that it survive the subsequent coating (and quenching) processes as well as the stamping and assembly processes without cracking or delaminating. This was accomplished in part by maintaining good corrosion resistance at low film thickness³. When the automobile industry adopted the use of zinc protection on both sides of the coil coated sheet, the proprietary chromated zinc-rich system became less competitive with electrogalvanized steel. The use of the latter has not largely surpassed the specialized proprietary coating system except in some limited one-side-coated sheet applications. Apart from these applications and some specialty applications in Europe (fencing), the large volume use of the proprietary zinc/chromate-complexed coating system for automobile body parts is now a thing of the past.

Physical Aging Effects: Densification

Both the rate of cooling and the interval between the cooling and post-forming processes affect the resistance of the applied film to cracking on deformation. A film rapidly cooled through the Tg will retain more free volume than a similar film cooled slowly. Therefore, there is a greater opportunity for improved conformational adjustment towards a reduced free volume condition after

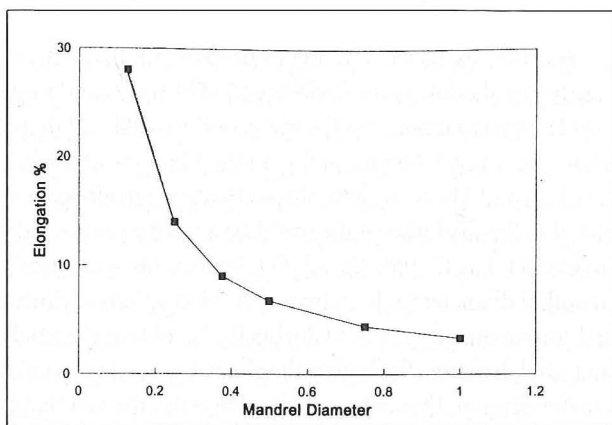


Fig. 2

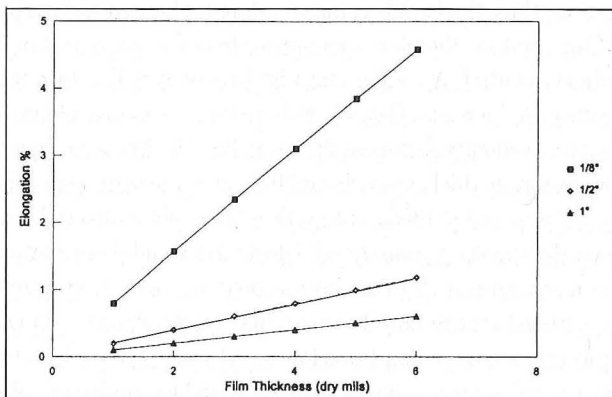


Fig. 3

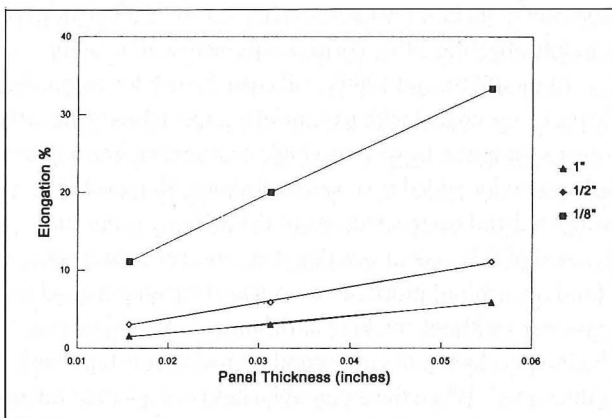


Fig. 4

Fig. 2. Effect of Mandrel diameter (in inches) on percent elongation (ASTM D 522). 1 in. = 25.4 mm. Derived from data in ASTM D 522.

Fig. 3. Effect of coating film thickness on percent elongation (ASTM D 522). 1 mil = 25 micrometers. Derived from data in Reference 2.

Fig. 4. Effect of panel thickness on percent elongation (ASTM D 522). 1 in. = 25.4 mm. Derived from data in Reference 6.

cooling. Thus, a film cooled rapidly will exhibit greater flexibility and therefore greater resistance to cracking and de-adhesion than will a similar film cooled slowly. The effect is quite time dependent, however. Given sufficient time, the film cooled rapidly from curing temperatures will slowly achieve greater molecular compaction or densification and reach an equilibrium conformation at some ambient temperature below the T_g . At this stage, it will be quite as inflexible as the film cooled slowly.

The phenomenon, also known as physical aging, is illustrated by Port⁴. He describes 2 applications of the same pipe coating on 2 pipes, one with a heavy cross section and one thin walled. After curing, both pipes were quenched under identical conditions in cold water, sectioned and bent. The coating applied to the thick walled primer cracked, while the same coating on the thin walled primer did not. Repeated a day later, the same test resulted in both samples cracking. The effect is related to the greater heat retention properties of the thick walled pipe. The cooling of the coating was slowed during quenching, allowing a more complete adjustment towards conformational equilibrium (and release of free volume). The coating on the thin walled pipe cooled more rapidly. Therefore, it had less opportunity to adjust conformationally and to minimize free volume before passing through the T_g range. In this case, conformational adjustment occurred more slowly (overnight). This process results in eventual reduction in free volume and enough decreased flexibility to fail the second bend test.

Printed bottle caps and crowns are necessarily coated before final fabrication (essentially the sealing of the bottle). Because of this, they must be distortion-printed. This is a process in which the print design on the flat blank is deliberately distorted in such a way that during the crimping operation, the distortion is canceled and the desired image is created. During crimping, the coating must not crack or lose adhesion.

Interestingly, instances have been recorded where certain thermosetting coatings on such metallic bottle caps have spontaneously delaminated on the shelf months after fabrication. This seems likely to be a result of residual strain within the coating film. The strain arises from a degree of reversible deformation, which, when stress is removed, acts to oppose adhesion. After fabrication, the deformed condition of the film is maintained solely by the metal substrate, while the coating attempts to recover elastically. As the restoring force eventually exceeds the adhesion to the metal (possibly driven by the physical aging effects noted above or perhaps even hydrothermal effects), delaminations takes place. Improved resistance to this type of failure might be achieved by improving the adhesion of the coating to the bottle cap, reducing its film thickness, or replacing the coating with one that irreversibly deforms under the stress conditions of fabrication. Such spontaneous peeling may also be facilitated by interfacial insufficiencies between the coating layers. Again, it takes less stress on (or strain within) a coating to release a coating film when its adhesive strength is lowered. Coating release is facilitated by substrate contamination, defective metal treatment, or incompatible or otherwise faulty conversion coatings.

As Gaske⁵ reports, later processing or subsequent temperature changes may also induce failure in coil coatings that have maintained excellent integrity during the drawing operation. The coil coating industry employs a 54C (130F) "dry heat" exposure test specifically to assess this tendency.

Empirical Test for Formability

In addition to the cylindrical and conical mandrel test and the impact (rapid deformation resistance) tests, several other methods are commonly used for estimating the deformability of coatings.⁶

The ASTM D 522 mandrel test assesses flexibility by subjecting a coated panel to bending over mandrels of successively diminishing diameters (uncoated panel face against the mandrel). The lower the diameter over which the panel may be bent without cracking or delaminating the coating, the better the flexibility of the coating. Resistance to sudden deformation (ASTM D 2794) involves dropping a weighted indenter from increasing heights onto a coated panel. This action is continued until the indentation produced is sufficient to result in either cracking or delamination of the film. Indentation forces are expressed in inch pounds or kilogram-meters (a product of the indenter weight times the height through which the indenter falls). Lower values are obtained when the indenter impacts the reverse side of the panel (producing a convex dimple) than when the indenter impacts the coating directly and produces a concave indentation.

Typical specification for coil coatings differentiate between impact values producing fracture and those producing adhesive loss.⁷

A more common test of flexibility of coil coatings is the T-bend test (ASTM D 4145). In this test, the coated sheet is repeatedly folded back upon itself through 180 degrees using a suitably clamped die. The coated surface is on the outside of the bend. The first bend (OT) is the most severe. Subsequent bends, 1T, 2T, 3T, are made around the first bend, second bend and third bend. Made over successively increasing thickness of metal, these bends are, therefore, progressively less severe. The effect is analogous to increasing the mandrel diameter in ASTM D 522.

Coil coatings may also be evaluated by stamping tests, which provide rapid deformation of coated stock by drawing the

metal into cupped shapes at high rates of deformation. Cupping tests may be used to produce deformations at a slower rate.

In many of the above tests, cracks may be quite difficult to detect. Several techniques may be used to facilitate such recognition. These methods include the microscopic examination of the bend and chemical tests such as the painting of the site of deformation with acidified copper sulfate solution.

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