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# Acceleration of Amine-Cured Epoxy Resin Systems

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# Acceleration of Amine-Cured Epoxy Resin Systems

## Abstract:

The choice of accelerators for amine-cured epoxy formulations is sometimes done as an afterthought, using old accelerator compounds or packages designed for other purposes.   Such an approach to acceleration may eventually create problems in the final products that, in some cases, may never be traced back to the accelerator.  Properly used accelerators can be an integral part of fine-tuning the reactivity of slower reacting resin formulations and can also serve to beneficially influence properties such as glass transition temperature, modulus, strength, elongation at break, and chemical resistance.  In epoxy formulations that utilize amine curatives, accelerators typically increase the reaction rate by 1) adding, or quickly creating, hydroxyl groups, 2) increasing the heat generated (thus increasing the temperature) in the system, or both.  If acceleration alone were needed in all applications, one would just use the necessary amount of the fastest accelerator.  However, other factors, such as cost, toxicity, solubility, processing effects, final properties, regulatory concerns, ease of use, and amine-blushing mean that it can be advantageous to select specific accelerators that are well-matched to or designed for specific applications.

## Introduction:

The terminology used for accelerators is varied and may sometimes cause confusion since the terms accelerator, catalyst, promoter, initiator, dryer, etc., are sometimes used loosely even though they can apply to very specific types of materials having distinctly different characteristics and functions.  This article focusses on amine-cured epoxy resin systems and the term accelerator is used to describe a variety of compounds and mixtures used to increase the reaction rate, whatever the mechanism.  Over several decades, many papers have been published on epoxy accelerators [1, for example] with relatively few of them offering broad practical advice.  This paper is intended to provide a useful basis of understanding various ways of increasing the curing speed of epoxy systems while avoiding the confusion and pitfalls that may arise due to unexpected effects that can occur when accelerators developed for certain applications or curing conditions are used in very different circumstances.  The dual purposes of creating easily made formulations and designing experiments to highlight fundamental trends can be at odds with one another, though in this work addressing both needs is attempted.

The choice of accelerators for amine-cured epoxy formulations has often been done as an afterthought, using old accelerator compounds or packages designed for other purposes.   Such an approach to acceleration can create problems.  This can occur, for example, when compounds like tris-(dimethylaminomethyl) phenol (a.k.a. DMP-30) or benzyl dimethylamine (a.k.a. BDMA or dimethylbenzylamine) are used with amine curing agents rather than anhydride curing agents. These materials can create issues of odor, handling, yellowing, brittleness, and/or $T_g$ (glass transition temperature) loss. It may also be that epoxy homopolymerization caused by such accelerators can limit some types of mechanical performance. Problems may be avoided or minimized by carefully evaluating and choosing from among the various accelerators available in the marketplace.

Accelerators typically increase the reaction rate of epoxy systems by 1) adding, or quickly creating, hydroxyl groups, 2) by increasing the heat generated (thus increasing the temperature) in the system, or both. If only acceleration mattered, one would just use the necessary amount of the fastest accelerator. However, other factors, such as cost, toxicity, solubility, processing effects, final properties, regulatory concerns, and ease of use, mean that it can be advantageous to select specific accelerators that are well-matched to particular applications. For instance, careful pairing of accelerators with slowly reactive polyetheramines may allow the use of higher processing temperatures, thereby decreasing the need for epoxy diluents that may decrease thermal and mechanical performance properties and increase cost. Properly chosen accelerators, and their use levels, can be an integral part of fine-tuning the reactivity of epoxy systems and can also serve to beneficially influence properties such as glass transition temperature, modulus, strength, elongation at break, and chemical resistance. Accelerators well-suited to some applications, like composite molding, may not fare as well in other applications such as ambient-cure floor coatings.

## Accelerators Can Increase Options for Resin Choice and Processing

Standard liquid epoxy resins (such as ARALDITE® GY 6010 epoxy, EPON® 828 epoxy, D.E.R.® 331 epoxy, etc.) all contain low levels of hydrolyzed epoxy groups (i.e. glycol end groups) which serve to 1) increase the reactivity of the resins toward amine hardeners, 2) greatly increase viscosity of the resins, and 3) prevent crystallization of the resins. The hydrolyzation is readily done at the end of the resin production process using acid and heat. Over time, such partially hydrolyzed DGEBA resins became the “standard bisphenol A epoxy” or “liquid epoxy resin (L.E.R.)” type resin, as it met the requirements of the broadest assortment of end-users.

Although these higher viscosity hydrolyzed resins are needed for some applications, other applications, such as the molding of large composites, greatly benefit from the use of lower viscosity, slower reacting non-hydrolyzed resins. In recent years bisphenol F diglycidyl ether resins (DGEBF), desirable for their lower viscosity (relative to DGEBA resins), have become more available and are often used as blends with lower viscosity, non-hydrolyzed DGEBA resins (e.g. EPON® 826 epoxy or D.E.R.® 383 epoxy) because each resin prevents the room temperature crystallization of the other resin. Several such blends are commercially available from various manufacturers. Such slower reacting resin formulations can benefit from the incorporation of accelerators. Furthermore, careful pairing of accelerators with slowly reactive amines can be used to fine tune formulations to allow the use of higher processing temperatures, thereby decreasing the need for expensive epoxy diluents that may decrease thermal and mechanical performance properties.

In nearly any manufacturing process that uses amine-cured epoxy systems there is a competition between increasing the reaction rate (to increase throughput and shorten the time to completion) and keeping the reaction slow enough to avoid: 1) running out of working time / pot-life, 2) premature gelation, 3) exothermic degradation, 4) deleterious part expansion / shrinkage, 5) off-gassing, etc. Accelerators can be used to fine tune the reaction rate of a resin formulation to a given process, thus striking a useful balance between working time and throughput. As might be expected, accelerators are most commonly needed and have the greatest effect in formulations that utilize slower reacting amines, such as polyetheramines. Polyetheramines, such as JEFFAMINE® amines, are often chosen because of the lower reactivity and the longer working times that they provide.

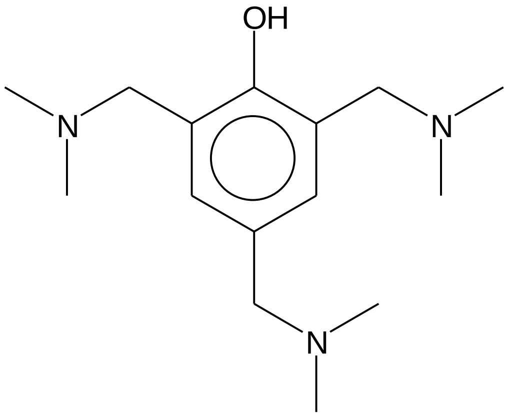
Methods for accelerating amine-cured epoxy systems may include the following: 1) increasing the temperature of the material or process, 2) increasing the reactive group concentration in the mixture by using lower EEW (epoxide equivalent weight) or AHEW (amine-hydrogen equivalent weight) components, 3) adding hydroxyl containing species (alcohols) or more quickly generating hydroxyl groups adding amine having higher reactivity, and 4) decreasing the pKa (increasing the acidity) of the added alcohols. Certain strong acids and salts have also proven effective, though those pairing tightly with amines can slow the epoxy reaction. Compounds which primarily promote epoxy homopolymerization are sometimes described as accelerators in the literature but these often cause a notable decline in mechanical properties and their use will not be discussed here.

## Non-reactive vs. Reactive Accelerators

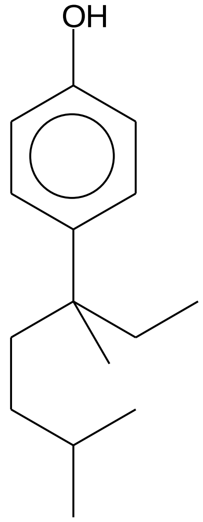
Use of non-reactive, hydroxyl containing accelerators such as alcohols can simplify curing speed adjustments in that when using them there is no need to recalculate the amine-hydrogen to epoxide stoichiometry of the system. Additional accelerator can simply be added until either the desired reactivity is achieved or until some performance characteristic of the process or cured epoxy declines to an unacceptable level, requiring further reformulation. Phenolic hydroxyls can be quite reactive with epoxide groups in the presence of particular catalysts (such as phosphonium salts) and at elevated temperatures but for the formulations described herein they are taken as non-reactive for stoichiometric considerations, as are aliphatic tertiary amines, when used in non-epoxy-rich formulations. Accelerators that fall into this category include mono-nonyl phenol (MNP), benzyl alcohol, and triethanolamine.

Tris-(dimethyl amino methyl) phenol, widely known in the marketplace as DMP-30 (now sold by several companies under various trade names) and benzyldimethylamine (BDMA) can also be considered non-reactive in systems having a 1:1 stoichiometry that are cured with no more than moderate heating. It has been reported however that when excess epoxide and/or high temperatures are used in curing, tris-(dimethyl amino methyl) phenol use may cause some epoxide homopolymerization. Also, it has been suggested that crosslinking of epoxies may occur through reaction of epoxide with the primary hydroxyl groups of triethanolamine when it is used to accelerate mixtures containing a stoichiometric excess of epoxide groups. However the evidence appeared un-compelling. The observed increases in $T_g$ may be related to the higher proportion of stiffer bisphenol A based segments in these fairly low $T_g$ polymers, in agreement with the Fox equation. [2]

Figure 1: Idealized Structures of Some Accelerating Compounds

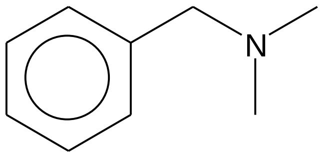


Tris-(dimethylaminomethyl) phenol

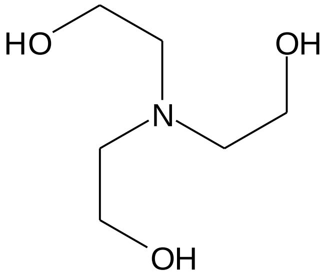


Nonyl phenol, various isomers

$C_{15}H_{24}O$ F.W. = 220.350



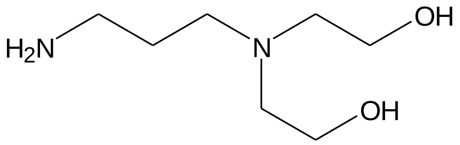
Benzyldimethylamine (BDMA)



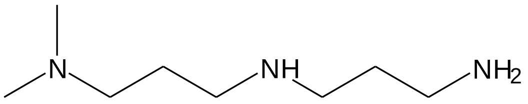
Triethanolamine

In contrast to these, the use of reactive accelerators may require recalculation of stoichiometry to maintain optimum long-term performance, particularly if the accelerator is less efficient and requires higher use levels, or when the AHEW of the accelerator differs significantly from that of the hardener. Reactive accelerators matching the AHEW of the amine hardener used have been previously described (Accelerator 60 and Accelerator 81, for JEFFAMINE® D-230 and JEFFAMINE® T-403 amines, respectively). [3] Such matching allows the substitution of the accelerator for hardener on a weight for weight basis since the stoichiometry is maintained. This is convenient since there is no need for recalculation each time a change in formulation reactivity is desired. There will typically be limits to increasing amounts of such substitution as the glass transition temperature and related properties change. One quick-reacting amine, APDEA (amino-n-propyldiethanolamine, Figure 2) has essentially the same AHEW as JEFFAMINE® T-403 amine and can thus be similarly substituted without recalculation of stoichiometry. In contrast one would need to recalculate the stoichiometry if one chose to use DMDPTA, with an AHEW of about 53.1, to accelerate the same amine.

Figure 2: Two Amines Used as Reactive Accelerators



APDEA
(amino-n-propyldiethanolamine)
$C_7H_{18}N_2O_2$ F.W. = 162.23
AHEW = 81.1



DMDPTA
(N,N-dimethyldipropylenetriamine)
(a.k.a. DMPAPA)
$C_8H_{21}N_3$ F.W. = 159.28 AHEW = 53.09

Two of the many possible methods of assessing the effectiveness of accelerators with respect to epoxy curing are mechanical dry-time testing of coating films and gel time testing of small cups of formulations. The resin formulations utilized here were not comprehensively evaluated but particular performance characteristics, both good and bad, were noted when readily evident. Additional tests are advisable to determine the suitability of these formulations for a particular application method and purpose.

In both types of tests there are variations due to uncertainty in measurement reading, laboratory temperature, test equipment, and other factors. Also, there naturally tends to be more uncertainty at longer measurement times since changes in airflow, temperature, and humidity may show more variability with time. The initial dry-time testing was done using accelerator levels of 5.0 phr, with the idea that the shorter gel times at this relatively high use level would be more consistent, thus allowing easier comparison, and that more data utility might be achieved if drying times were within the time frame of practical application.

## Experimental:

### Resin Systems and Accelerators Chosen

The epoxy resin utilized was a standard DGEBA liquid epoxy resin (ARALDITE® GY 6010 epoxy). This was formulated with either a polyoxypropylene di-primary amine having an AHEW of 60 (JEFFAMINE® D-230 amine), a polyoxypropylene tri-primary amine having and AHEW of 81 (JEFFAMINE® T-403 amine), or a polyoxypropylene tetra-primary amine having an AHEW of 83 (XTJ-616). Thus the curatives, in the absence of reactive accelerators, had nominal functionalities of four, six, and eight with respect to reaction with epoxide groups. All systems were formulated to ensure a 1:1 stoichiometric ratio of amine-hydrogen to epoxide groups, taking into account any primary or secondary amine groups present in some of the accelerators being evaluated. Accelerator 399 (Huntsman) is a partially reactive accelerator that provides both hydroxyl groups and highly reactive amine groups to increase reaction speed.

### Viscosity, Gel Time, and Exotherm Temperature Measurements

The method used for measuring gel times and maximum exotherm temperatures has been used at Huntsman for more than a decade. Though not following the ASTM method, several features of that method were incorporated. The method used is: 1) easy to run, 2) reasonably reproducible (best at faster gel times) and 3) has practical utility beyond that of methods using smaller (100 g) quantities of resin mixture. In this method 200 grams of room temperature resin system are weighed into a pint-sized metal paint can (friction lid type, no handle).The components are well-blended by hand for five minutes. (Time zero is when blending starts). The LV-4 (64) spindle of a Brookfield Model DV-II digital viscometer is inserted to the required depth in the center of the can, and the tip of a J-type thermocouple is positioned as closely as possible to the center of mass for temperature readings. The can sits on a one and one-eighth inch thick cork ring (3 inch diameter) for insulation of the bottom, inside a particular hood with a consistent sash height. The viscosity of the resin is periodically noted, as is the temperature. As the viscosity increases, the rotational speed of the spindle is decreased to keep it within the torque range recommended in the viscometer's instruction manual. When gelation is seen to occur, the spindle is immediately removed (prior to permanent embedment in the resin) and the temperature is further monitored until the maximum (peak) value has passed. The temperature of the lab air is also noted.

### Coatings for Dry Time Measurements

To limit weighing uncertainty, the total mass of the formulations mixed for drawing down coatings was typically between about 130 and 150 grams, depending upon the formulation. In preparing the coating formulations, the resin was pre-heated to 55°C to aid in thorough blending, thus minimizing the mixing time required. When preparing each formulation, the resin was weighed in first, followed by the amine curative, followed by the accelerator.
Smooth finish 3 x 6 inch, cold-rolled steel QD-36 panels from Q-Lab Corporation (Cleveland, Ohio), were used throughout as received. Three panels were placed, transversely, next to one another and held down using a magnetic panel holder. The film applicator used for drawing down the formulations by hand, had a fixed gap of 6 mils. (The three panels were designated, in order, as A, B, & C, where panel A was the first panel coated.) It was seen from previous work that the cured film thicknesses obtained using this method typically showed significant increases from panels A to B to C, which is a common effect related to the rheological behavior of the fluid being applied through the gap. To minimize the system to system testing error , two minutes of hand mixing was done by the same worker and the panels were drawn down by a different worker, taking care to achieve consistency. Panels A were usually about 3 mils (0.076 mm) thick whereas panels C were nominally 5.5 mils (0.14 mm) thick. Panels B, the center panels, were not tested for dry time, but set aside for possible other purposes except in two instances where panel A was not used due to issues of wetting consistency.

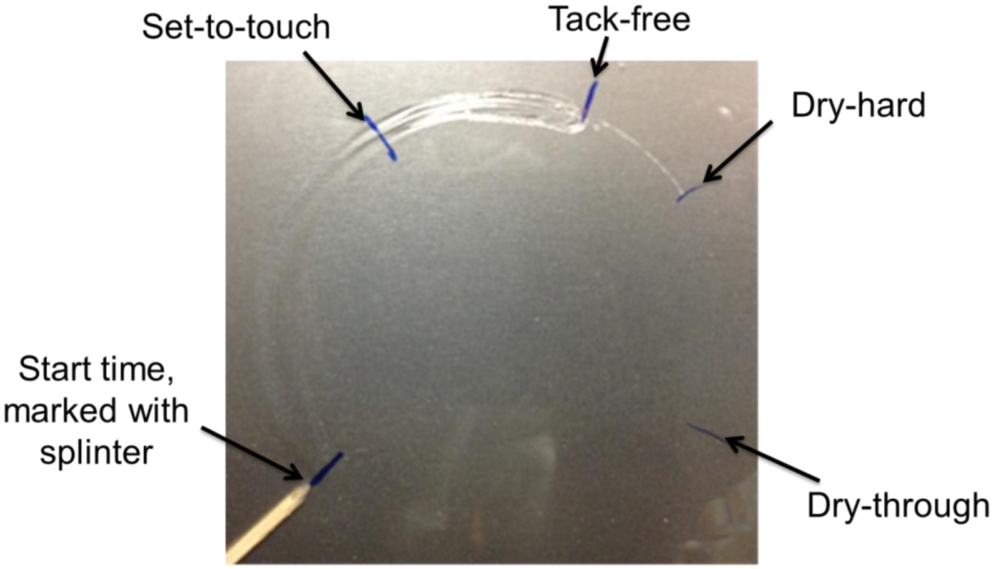
Gardner circular drying time recorders were used in a corner of the laboratory free from drafts and having a nominal temperature of 22-23°C and a nominal humidity level of 59-63%. The different stages of drying were assessed using the terminology in ASTM D 5895 ("Standard Test Methods for Measuring Times of Drying or Curing During Film Formation of Organic Coatings Using Mechanical Recorders). A summary of drying terms used both in the standard and in the data tables, in chronological occurrence, is as follows:

"Set-to-touch time" is reached where a pear-shaped depression appears in the film when the film stops flowing over the path of the recorder's stylus and leaves a track in the film.

"Tack-free time" is reached where the continuous track in the film ceases and the stylus starts to tear the film or leave a discontinuous cutting of the film.

“Dry-hard time” is reached when the stylus stops tearing or cutting the film, but leaves only a visible trace on the film.

“Dry-through time” is reached when the stylus no longer leaves any visible track on the film. Additional variability is expected for this measurement since the visibility of minor marking is highly dependent on the light source, angle of viewing, and the eyesight of the observer. Rotation and tilting of the panel under the light source can aid in the determination.



## Data and Discussion:

### Measuring the Efficacy of Accelerators

The criteria for assessing whether the cure speed of a given epoxy system is suitable for use can differ greatly by end-use. As an example, the curing profiles of epoxy formulations used in coatings and composite applications are very different. Many composite applications, such as resin transfer molding processes, have little or no air exposure and the reaction exotherms can greatly increase the temperature, particularly in thick regions. Such temperature increases can affect both processing options and the final properties of the part. In contrast, epoxy coatings typically have much air exposure during curing and show little or no temperature rise once applied. Because of such differences between end-uses, accelerators that perform poorly in one application or test may do well in another. Such is found to be the case when highly reactive accelerators, useful for composite systems, cause blushing in coatings, thus lengthening or preventing drying.

In the work presented here we assessed the reactivity of several accelerators using two common types of tests: 1) dry time measurements of coated panels and 2) gel time, temperature, and viscosity measurements of 200 grams of formulation. The results of these tests will be separately discussed.

## Coating Dry Times

Regarding epoxy coatings, the question “Is it ready?” can be about whether it’s ready for final use, or whether it’s ready for the next coat. The suitability of certain accelerators for coating applications will hinge upon whether the coatings are baked or not. Non-baked coatings are common, such as those used for flooring. Applicators of floor coatings need to maintain sufficient pot-life (working time) for application yet have fast enough curing that the area can be quickly placed back into service, withstanding the effects of use, without marring. Ambient temperature curing is typical and seasonal variations in temperatures are often dealt with by adjusting the formulations, with winter formulations having higher reactivity than the summer formulations. At cooler temperatures, care must be taken that blushing is not induced by either the type or the usage level of the different hardener blend or the chosen accelerators.

It’s useful to recognize that accelerators may function in multiple ways. As an example MNP (mono-nonyl phenol), which is still widely used in many parts of the world, is an excellent accelerator for amine-cured epoxy systems. Additionally, in flooring, decoupage, and doming resin applications, where use levels can reach 40-65 phr (parts per hundred parts of resin), MNP also plasticizes the formulation enough to allow a high degree of cure (crosslinking polymerization) at ambient temperatures. For systems cured at ambient temperatures, sufficient polymerization to develop the required properties will not occur if the glass transition temperature of the system is too high, since the rigidity of very glassy materials does not allow the molecular mobility needed for additional reaction. For amine cured systems then, higher amine stiffness and functionality will require higher levels of plasticizer in order to reduce the glass transition temperature and allow sufficient property development. The degree to which accelerators can provide a useful level of plasticization thus depends upon both their use level and upon the underlying glass transition temperature of the formulation in which they are used. Due to the inherent reactivity differences of many accelerators, the use levels needed to match reactivity of one accelerator with another (for substitution) may vary significantly. Thus in ambient cured epoxy coatings, formulators must walk a fine line between having the coating plasticized enough for sufficient property development but not so much that the $T_g$ drops too far and the coating’s hardness is no longer sufficient.

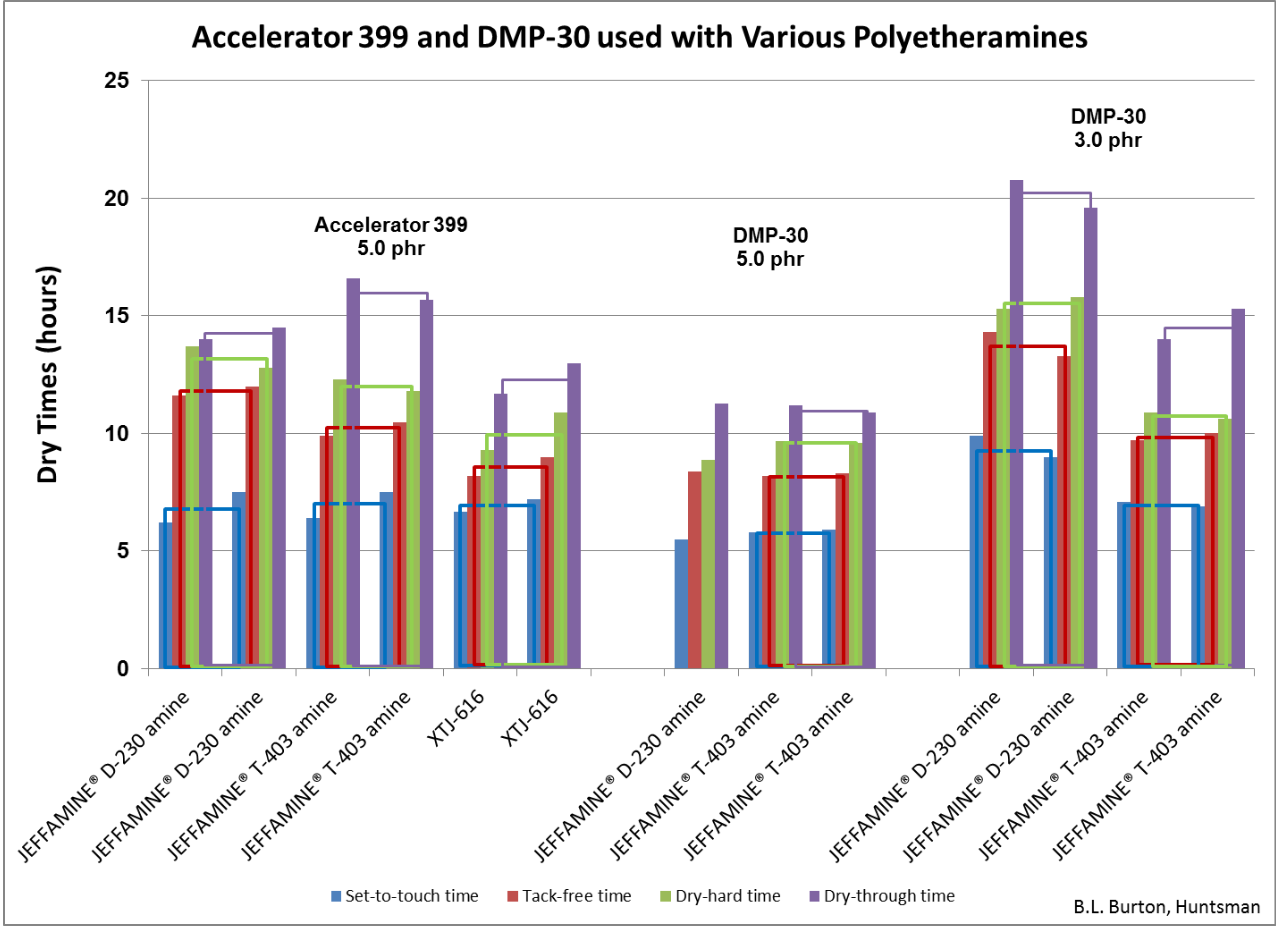
Increased coating hardness, a fairly common goal, is often achieved by making changes that increase the glass transition temperature of the coating in those cases where the $T_g$ is too low. A good way to do this for formulations containing fairly high levels of non-reactive accelerators, like MNP or benzyl alcohol, is to remove a portion of these plasticizing accelerators. However, if too much is removed and the ultimate $T_g$ of the formulation becomes too high, unreacted epoxy and amine groups will remain. These can lead to increased color, moisture sorption, swelling, and other undesirable effects. Alternatively, a common method of raising the $T_g$ to increase hardness is to substitute an amine having a more rigid molecular structure (and therefore a higher $T_g$ capability) for an amine with a more flexible structure. This has been a standard practice for years by those using polyetheramine hardeners in decoupage coatings.

Figure 3 shows a comparison of Accelerator 399, an accelerator containing both hydroxyl groups and reactive amines, and DMP-30 when used to accelerate polyetheramines of differing functionality: four (“D-230”), six (“T-403”), and eight (XTJ-616) amine-hydrogens per molecule. In this, and in the subsequent dry time figures, pairs of columns are shown for nearly all coatings. The columns in the left set of each data pair represent data from the thinner panel A coating and the columns in the right half of each pair represent data from the thicker panel C coating. The similarly colored lines joining each half of a given pair of columns is a visual aid the viewer in comparing averages across systems while helping maintain a sense of the variability in the measurements.

Although DMP-30 containing coatings at a usage level of 5.0 phr showed shorter drying times than did Accelerator 399 containing samples, reduction of the DMP-30 level to 3.0 phr extended the dry times considerably. For the JEFFAMINE® D-230 amine formulation, the dry time of the DMP-30 accelerated coating is now longer (vs. 5.0 phr Accelerator 399) but the JEFFAMINE® T-403 amine formulation still shows DMP-30 to dry a little more quickly.

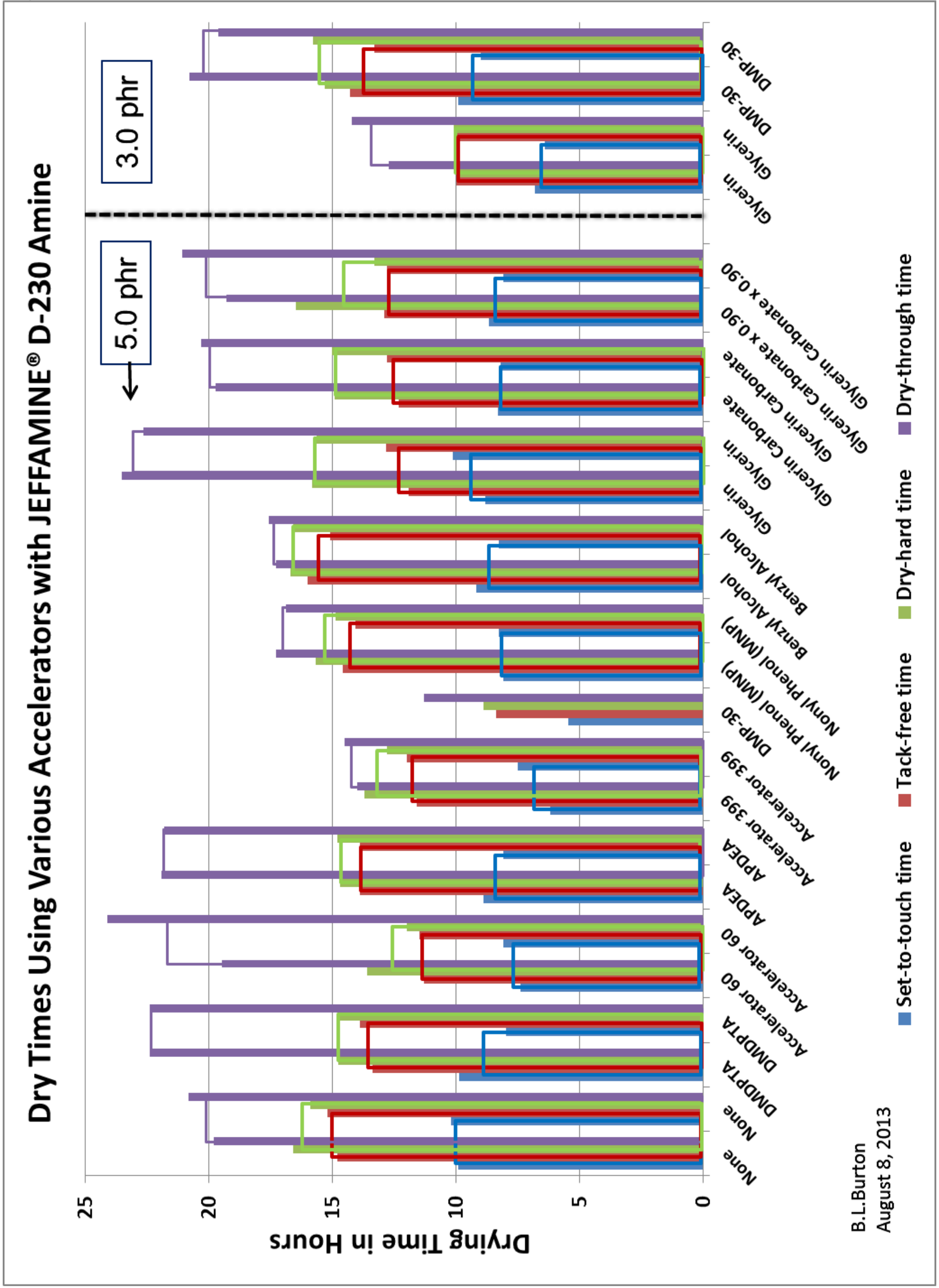
Looking across the data, no consistent trend of drying with respect to coating thickness is observed and most values of a given pair of A & C panels show relatively little variation. Focusing on the data to the left side of Figure 3 (5.0 phr Accelerator 399), the set-to-touch time appears unaffected by the change in average functionality of the amine hardener but both the tack-free and dry-hard times appear to decrease as functionality is increased. The DMP-30 containing samples, accelerated by phenolic hydroxyls, do not consistently show a trend.

Figure 3:



In Figure 4, JEFFAMINE® D-230 amine is used with a variety of accelerators at a 5.0 phr use level and also at 3.0 phr (far right side of the figure) in the case of glycerin and DMP-30. Note that control coatings (far left side, having no accelerator) have longer dry times than most systems, as might be expected, but are seen to have shorter dry-through times than coatings made using glycerin, DMDPTA, Accelerator 60, or APDEA. This appeared to be due to tackiness and/or softness of those coatings, caused by some combination of surface blushing and low $T_g$, respectively.. To check this, two accelerators, glycerin, which showed surface tackiness at 5.0 phr, and DMP-30, which did not, were subsequently tested at levels of 3.0 phr (right side of the figure). At 3.0 phr the glycerin containing sample, which was no longer tacky, now dried much faster than the control sample whereas the DMP-30 containing sample, which was not tacky at 5.0 phr, now had extended dry times, all being much longer than glycerin. Note that glycerin provides a much higher concentration of hydroxyl groups than does DMP-30 for a given phr level.

Figure 4:


Dry Times Using Various Accelerators with JEFFAMINE® D-230 Amine
5.0 phr
3.0 phr
Drying Time in Hours
0
5
10
15
20
25
None
None
DMDPTA
DMDPTA
Accelerator 60
Accelerator 60
APDEA
APDEA
Accelerator 399
Accelerator 399
DMP-30
Nonyl Phenol (MNP)
Nonyl Phenol (MNP)
Benzyl Alcohol
Benzyl Alcohol
Glycerin
Glycerin
Glycerin Carbonate
Glycerin Carbonate
Glycerin Carbonate x 0.90
Glycerin Carbonate x 0.90
Glycerin
Glycerin
DMP-30
DMP-30
Set-to-touch time
Tack-free time
Dry-hard time
Dry-through time
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These results raised the question of whether the other systems that appeared slower than the control system might also have faster final stages of drying if the accelerator levels were reduced.  This was indeed found to be the case, as illustrated by the data in Figure 5.  Note that even the earliest stage of drying, “set-to-touch”, appears similar or faster for the systems at the lower phr level. This may be explainable in that once enough accelerator is added to a system to have the accelerating hydroxyls readily available for catalysis of the epoxide groups’ reaction, further addition only serves to dilute the concentrations of reactive groups.  Such an observation was made years ago for systems using high levels of MNP.

Figure 5:  Accelerators showing lengthened dry times at higher use levels.

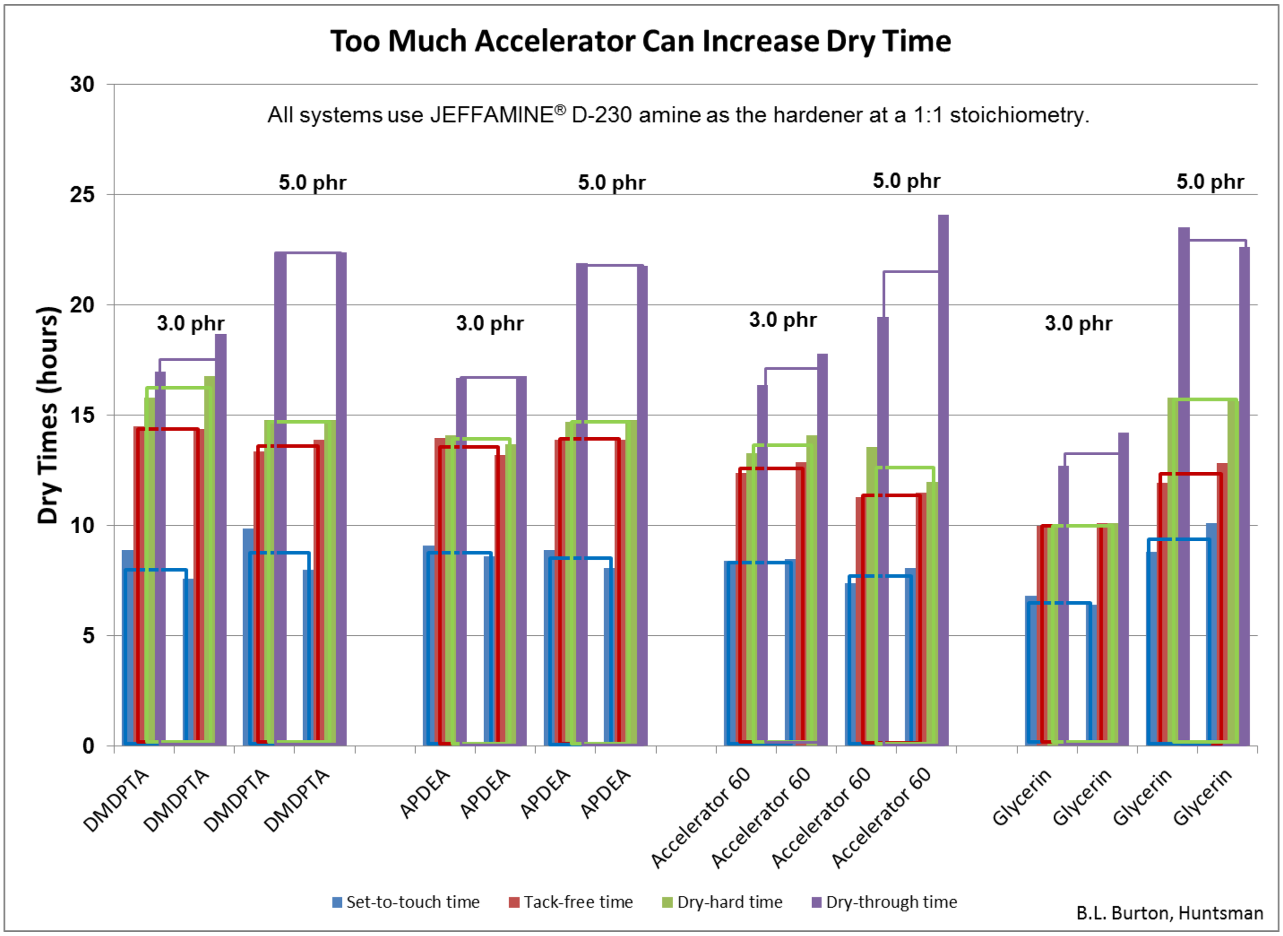
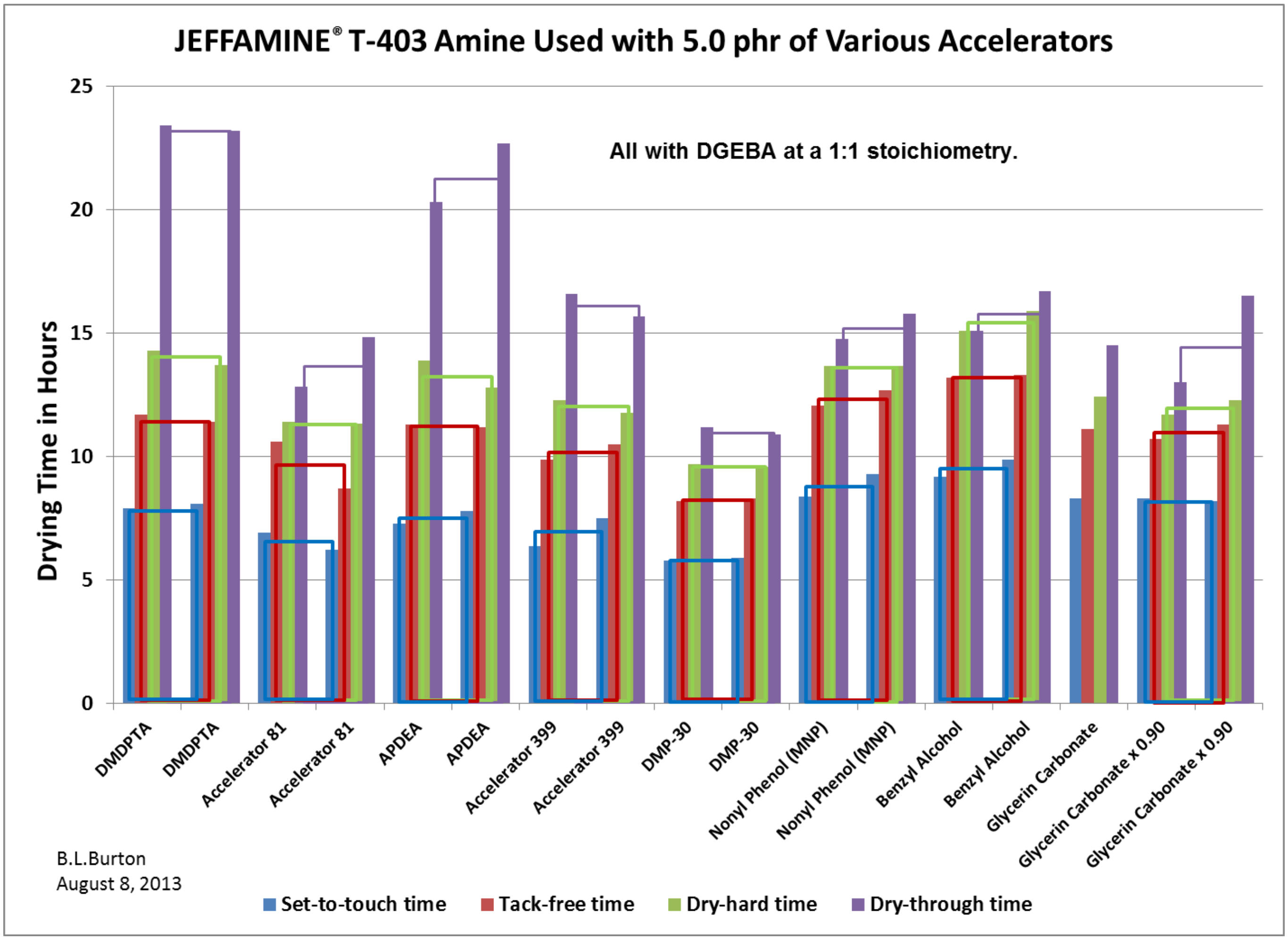


Figure 6 shows the results of using 5.0 phr of eight different accelerating compounds in a system where JEFFAMINE® T-403 amine is the hardener.  As before, variations between the thick and thin coatings of each pair appear minimal and show no consistent trend.  In this set of data, Accelerator 81 is used because of its AHEW of 81 matches that of the hardener.  Compared to the JEFFAMINE®

D-230 amine cured systems, JEFFAMINE® T-403 amine sometimes shows faster dry times, possibly due to some combination of the higher functionality of the amine and the lower actual weight percentage accelerator use levels (since the AHEW of the hardener is higher). Glycerin carbonate, the stoichiometric effect of which cannot be exactly calculated, was used at two different levels: one postulating that the carbonate would react only with primary amines and then 90 percent of that level. Essentially the same dry times resulted, which were reasonably fast. The ease of handling glycerin carbonate may be attractive for some formulators. Because its reaction with primary amines removes two amine-hydrogens per molecule from the formulation, it may serve to better plasticize formulations, which in certain applications such as flooring may provide an additional benefit. Additionally, it is expected to show lower levels of extractables in the cured coatings than do non-reactive accelerators like the phenolic compounds used or benzyl alcohol. It's interesting that the dry-through times with this accelerator are considerably shorter than when JEFFAMINE® D-230 was used.

Figure 6: Dry Times of JEFFAMINE® T-403 Amine with DGEBA and 5.0 phr of Various Accelerators



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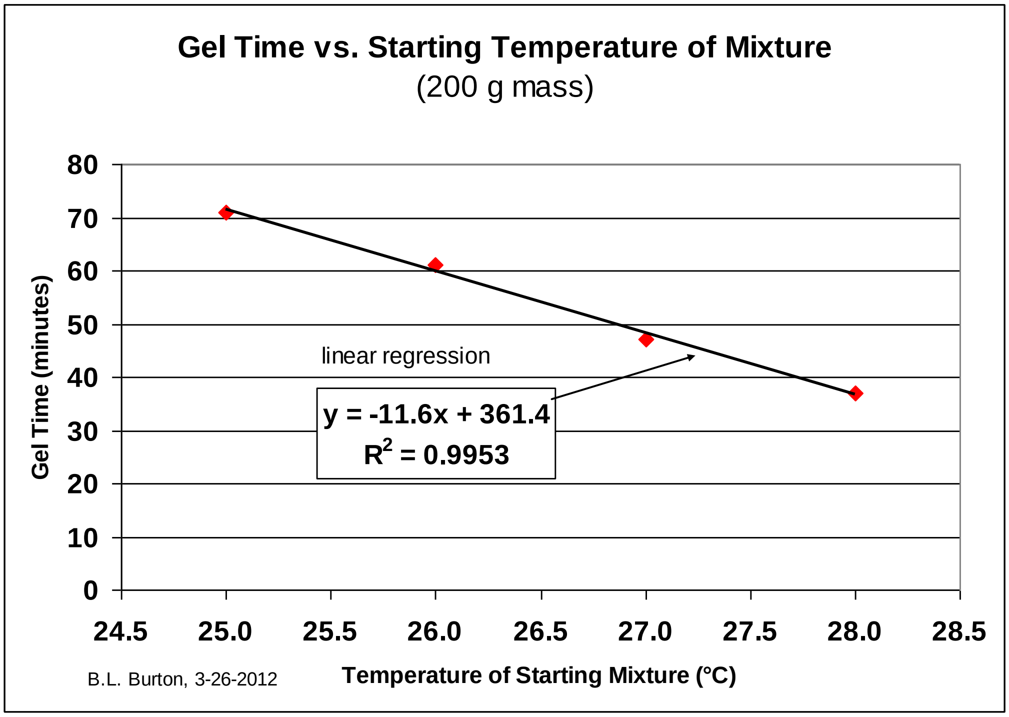
## Gel Times, Exotherm Effects, and Composites

Among the characteristics that can differ greatly between coating and composite applications is the degree of temperature rise in the material due to curing exotherms. Gel times are very sensitive to temperature, with only a few degrees difference in laboratory temperature causing significant gel time differences. In an effort to reconcile gel time differences between laboratories in which the same method was used (described in the experimental section), measurements were repeated on systems having very similar cycloaliphatic amines, with a range of 34-39.5 AHEW due to oligomer content variations. The gel time results are shown in the following table and figure. It thus appears that only a degree or two of variability of the mixture's starting temperature affected the gel time by about 24 percent for this blend.

Table 1: The Gel Time and Starting Temperature Data Plotted in Figure 7

| Gel Time (min.) | Starting Temp., °C |
|---|---|
| 37 | 28 |
| 47 | 27 |
| 61 | 26 |
| 71 | 25 |

Figure 7:



This illustrates the importance of consistent mixing when doing such testing since the speed and duration of mixing will affect the temperature of the reactive blend. The effect of mass size on gel time and peak exotherm temperature is also large. When evaluating and comparing accelerators, very different rank orderings may be obtained from gel time testing (often done on 100-200 gram masses) and dry time testing of coatings, particularly if some systems begin to form amine-blush from reaction with atmospheric carbon dioxide [5]. For gel time testing of more reactive systems, a mass of 100 g vs. 200 g (200 g used in this work) can mean the difference between the resin turning a bit yellow and turning black with cracking and smoking. Similarly, the use of higher mixing temperatures and/or higher accelerator levels can lead to thermal degradation. Lack of awareness of these effects has been responsible for calls to fire departments by neighbors of epoxy formulators. Since higher accelerator use levels can cause large increases in exotherm temperatures, lower mold temperatures may be needed when accelerator use levels are increased. How far one can push such limits will be dependent upon both part geometry and the materials used.

Even well below thermal degradation temperatures, problems can be created by increases in exotherm temperature caused by raising the amount of accelerator used. The amount of shrinkage upon cooling depends in part upon the relationship between the exotherm temperature, the mold temperature, and the glass transition temperature of the cured (or nearly cured) resin. Most cured, unfilled, epoxy systems have similar coefficients of linear thermal expansion (CLTE) when measured in the glassy state (i.e., below $T_g$). For unfilled systems, curvature of the thermal expansion line (from thermal mechanical analysis, TMA) is evident below $T_g$ but typical values averaged over a few decades are in the range of 60-65 ppm per °C. In contrast, when in the rubbery state (i.e. at temperatures above $T_g$) the CLTEs are often two to four times higher, with the higher values occurring for the lower $T_g$ systems. [4] Because of the greater CLTE of the cured epoxy when in the rubbery state, it’s possible that materials and processes producing higher exotherm temperatures could shrink less if the exotherm limited and utilized to increase the $T_g$. For accelerator usage, the practical effect would be that higher accelerator use could be beneficially paired with lower molding temperatures. If accelerator use drives exotherm temperatures beyond what may enhance full curing, the residual stress built into the composite may increase, harming the composite’s mechanical performance.

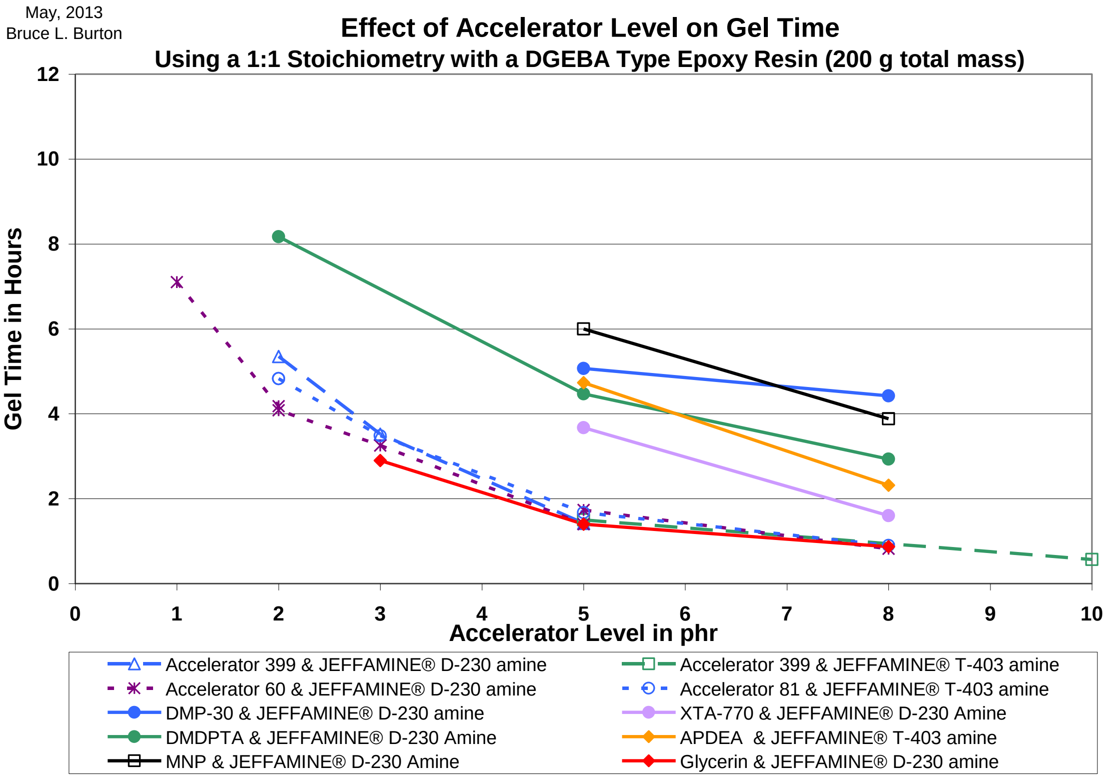
## Gel Time Data

Though in some ways DMP-30 (tris-(dimethylaminomethyl) phenol) is not a particularly good accelerator for amine-cured epoxy systems, its early placement in the market (more than 47 years ago) has aided it in retaining preference among many customers globally. Multiple companies sell DMP-30 under their own trade names, such as ARADUR® 960-1 catalyst (Huntsman), and K-54 accelerator (Air Products). It is speculated that its early adoption for use in amine-cured systems was due to its excellence in accelerating anhydride cured epoxies. To address customer requests for alternatives to DMP-30, gel time data for systems containing two use levels of this compound, 5 and 8 phr, were generated. These data are plotted in Figure 8 (solid blue line and circles) along with previously published data [3] and new data for systems containing nonyl phenol, glycerin, APDEA, DMDPTA, and XTA-770. When using the last three compounds, which are reactive accelerators, hardener use levels were adjusted to maintain a one to one stoichiometry of amine-hydrogen to epoxide groups. The relatively low efficiency of DMP-30 as an accelerator is evident from Figure 5. Additionally, in some operations its use is widely known to impart an undesirable odor, and increased photo-yellowing of some systems using it has been observed.

Because industry is used to working with these materials in terms of phr (parts per hundred of epoxy resin), this is how the systems were presented. However, such data can sometimes be misinterpreted since the weight percentages in the final systems vary as hardeners with different AHEWs are utilized. Glycerin, as might be expected based on its hydroxyl equivalent weight, is the most efficient of the accelerators evaluated, closely mimicking other hydroxyl rich accelerators like Accelerators 399, 60, and 81. Of the accelerator types containing only fast amines (XTA-770, DMDPTA, and APDEA, by which hydroxyl groups are generated quickly after mixing) the expected trend is supported, namely that lower AHEW compounds are more efficient accelerators. The two phenolic containing accelerators, DMP-30 (tris-(dimethylaminomethyl) phenol) and MNP (mono-nonyl phenol), are the least efficient. Note that more complete data for some of the compounds measured at two use levels would have significant curvature at lower use levels, thus it’s not appropriate to draw conclusions based extrapolations from high use levels. The slower materials were only evaluated at high use levels since the utility of the data beyond five or six hours is meager.

The reactive accelerators XTA-770, DMDPTA, and APDEA appear less efficient than the partially reactive, hydroxyl-rich accelerators Accelerator 399, Accelerator 60, Accelerator 81 or glycerin. The high efficiency of these latter materials suggests that in at least some applications, such as composites, better property retention could be realized since use levels could be lower. As previously illustrated however, their use in coatings systems at higher levels could be complicated by blushing issues.

Figure 8:

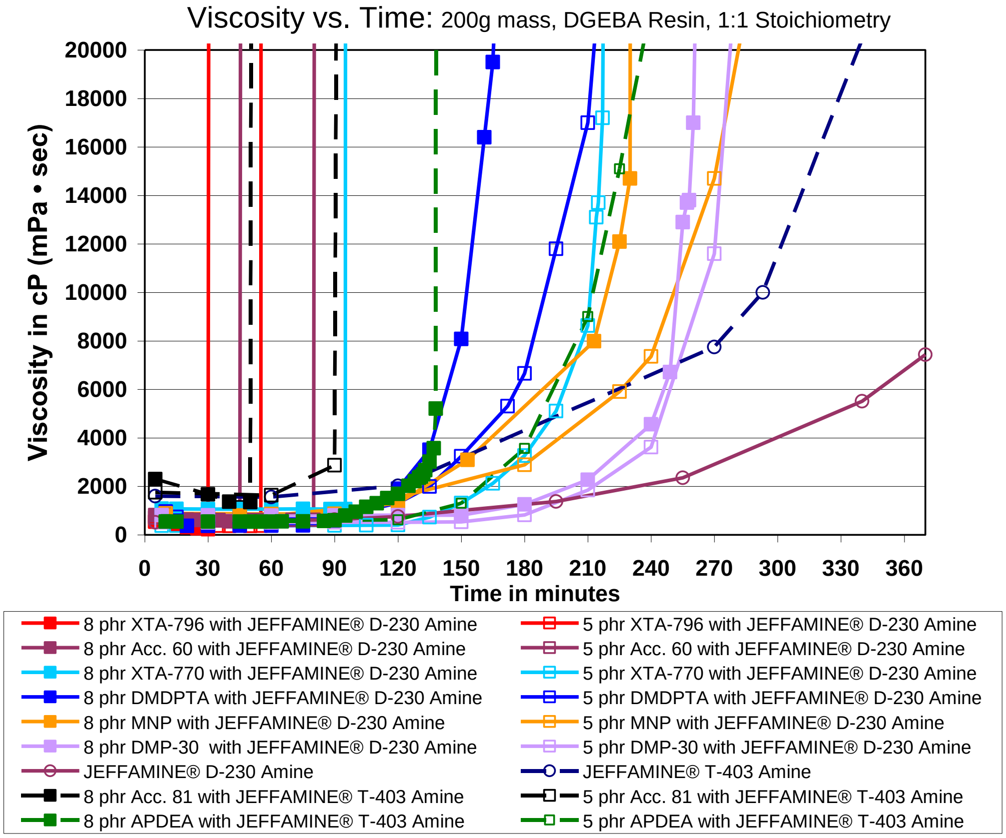


During the course of gel time testing, viscosity vs. time data were compiled for several different accelerators. In Figure 9, a standard DGEBA type liquid epoxy resin is used at a calculated one to one stoichiometry with the amine or amine plus accelerator combination. In this figure, solid lines indicate that the primary curing agent is JEFFAMINE® D-230 amine and dashed lines indicate that the primary curing agent is JEFFAMINE® T-403 amine. The legend listings are roughly in order of fastest to slowest except that the JEFFAMINE® D-230 amine listings come prior to the JEFFAMINE® T-403 amine listings. Note that of the accelerators listed in this figure, XTA-796, which is essentially a variant of and stand-in for Accelerator 399, gives the shortest gel times. It is followed by Accelerators 60 and 81, each of which are known to give better $T_g$ retention and have the advantage of allowing a weight for weight substitution with the primary polyetheramine hardeners used, thus allowing mixture ratios to remain constant and for the elimination of stoichiometric calculations when substitutions are made. Many customers find this desirable. XTA-770 (turquoise blue lines) is the next fastest accelerator and shows the greatest difference in gel times at the two levels shown. This is attributed to the relatively low AHEW of this accelerator (43) which means that increased use levels with higher AHEW primary amines leads to an increased concentration of reactive groups, thus the accelerating ability of XTA-

770 with the polyetheramine is synergistically enhanced as use levels are increased.

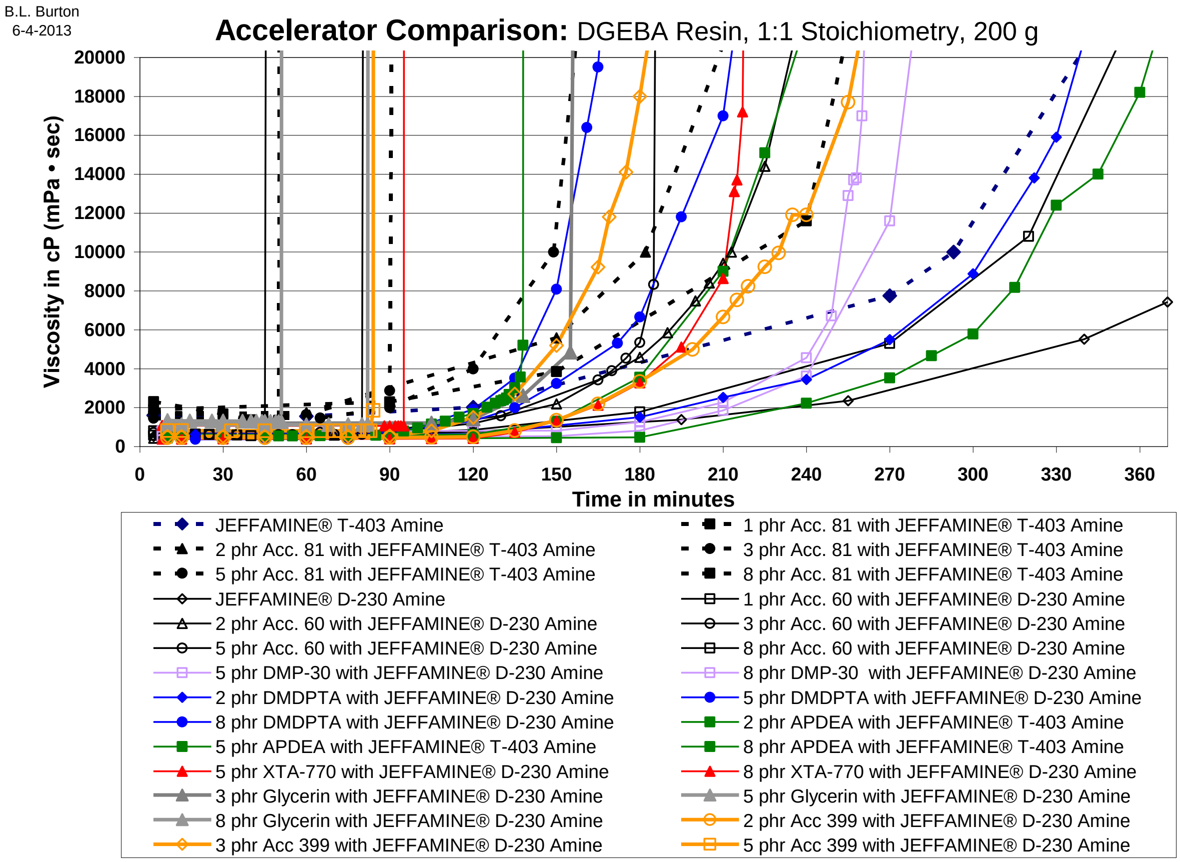
Figure 9:

B.L. Burton
5-29-2013



Data presented in Figure 10 serve to further illustrate the effects of various amines and accelerator use levels on viscosity and gel time, all done with the relatively slow reacting polyetheramines. A similarly wide set of curves exists for faster reacting amines, such as the ethyleneamine derivatives (N-aminoethylpiperazine (AEP), diethylenetriamine (DETA), triethylenetetramine (TETA), etc.) which, although already fast, can easily be further accelerated.

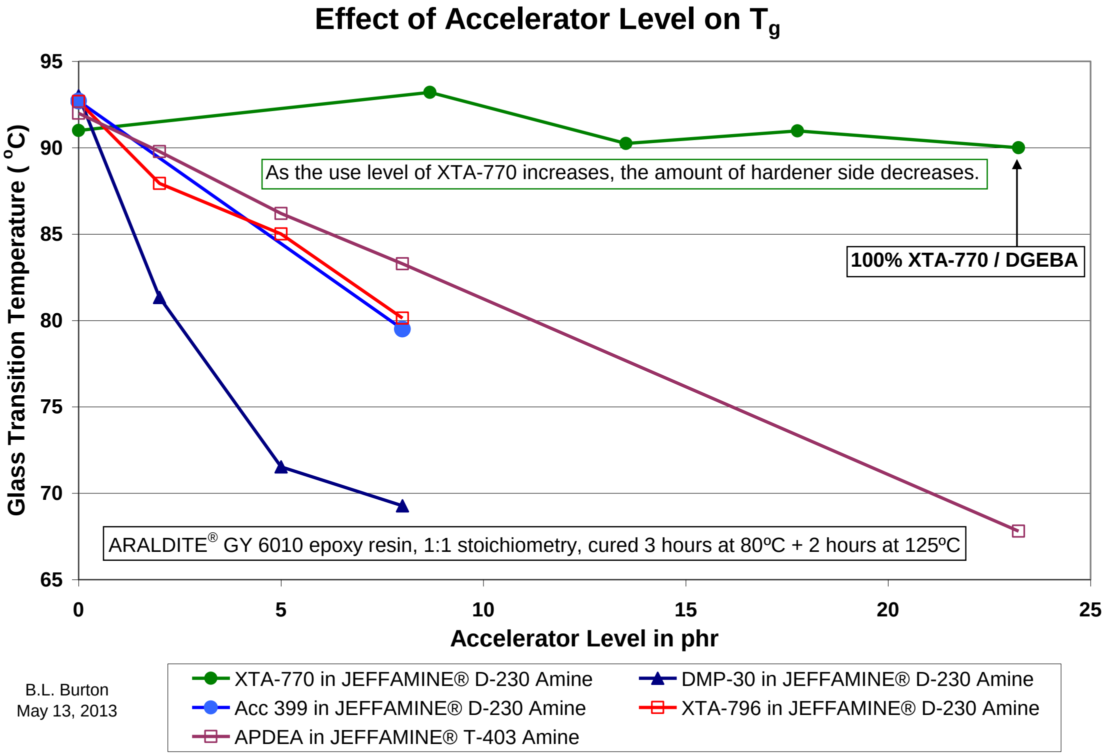
Figure 10:



DMP-30 (tris-(dimethylaminomethyl) phenol and MNP (mono-nonylphenol) results are represented by the lavender and orange lines, respectively. These are the only two phenolic hydroxyl containing accelerators evaluated. The accelerating effect of DMP-30 is readily attributed to the phenolic group rather than the tertiary amino groups given that phenolics have long been known as excellent accelerators and the use of BDMA (benzyl dimethylamine) with polyetheramines produced no useful effect (unpublished work by David Lewis). Even though MNP is widely used at high levels in many flooring applications and is well-known to limit or eliminate blushing (which is often the primary issue when curing in cool, damp environments), its effect at lower usage levels and its direct comparison with DMP-30 do not appear to have been previously reported. The fact that MNP appears to give slightly faster gel times at similar use levels may result from its slightly lower molecular weight of 220 g/mole vs. 265 for DMP-30. Note that the MNP structure depicted in Figure 1 has a highly branched aliphatic chain. Linear chain structures, sometimes found in the literature, are based on invalid assumptions.

The effect on $T_g$ for a selection of these accelerators is shown in Figure 11 for a standard liquid epoxy resin cured using the polyetheramine JEFFAMINE® D-230 amine at a one to one stoichiometry. Data on APDEA (aminopropyl diethanolamine) were generated using JEFFAMINE® T-403 amine due to the previously mentioned interest in matching AHEWs of accelerators to amine hardeners. The APDEA was substituted on a weight for weight basis without recalculating the mixture ratio. Because it functions as a crosslinker, APDEA can be used over the entire span of substitution, unlike non-reactive accelerating compounds. As shown in the figure, the $T_g$s decline with increased APDEA substitution though even at 100% replacement of the polyetheramine the $T_g$ remains high enough to have useful hardness. In contrast, the relatively fast amine curative XTA-770, used to accelerate JEFFAMINE® D-230 amine while changing mixture ratios to maintain a one to one stoichiometry shows no significant $T_g$ loss since its cured $T_g$ matches that of the polyetheramine used.

Figure 11: The Effect on $T_g$ with Increasing Accelerator Usage



## Summary and Conclusions:

1) Accelerator screening methods should be chosen according to the application / end-use since the curing behavior of coatings and bulk samples is very different.

2) The effect of a nominal 3-5 mil thickness variation on the dry times of un-pigmented coatings appeared negligible for most systems studied.

3)  At higher use levels, which may cause blushing or excessive plasticization of the coating (resulting in tackiness or softness), some hardeners will give longer dry times than if less accelerator is used.  Restated, sometimes less accelerator gives faster dry times.

4)  APDEA and DMDPTA, which can serve as curing agents as well as accelerators, performed well as measured by gel time testing but had extended dry-through times in coatings, even though early drying stages were fast, when measured at 5 phr.

5)  Glycerin carbonate provided excellent acceleration and coating appearance when used at levels of 5.0 phr.  Glycerin gave a tacky coating surface when used at 5.0 phr but gave excellent coating appearance at a 3.0 phr use level.

6)  A pair of hardeners yielding the same cured $T_g$ with DGEBA can be blended in any weight ratio to vary reactivity while maintaining that $T_g$ in the cured formulation.  (XTA-770 and JEFFAMINE® D-230 amine)

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