Catalyst Effects Found in Thermal and Mass Spectrometric Analyses of Polycarboxylic Acids Used as Durable Press Reactants for Cotton*

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SYNOPSIS

Effective polycarboxylic acids (PCAs) crosslink cotton cellulose by an ester linkage and smooth-drying fabrics are produced. The presence of a catalyst improves the crosslinking reaction. A series of seven PCAs was examined by thermal analytical (TA) and mass spectrometric (MS) techniques. The focus of this research was to discover if catalyst effects were measurable by TA and MS and to seek additional support for a proposed mechanism of cellulose/organic acid reactivity via acid anhydride formation. Thermal analyses consisted of differential scanning calorimetric (DSC) and thermogravimetric (TG) procedures. MS analyses, using the electron impact mode, were performed by direct probe sample insertion. Observed catalyst effects included shifts in peak positions to lower temperature/time, and were noticeable primarily in MS-reconstructed ion current chromatograms and DSC thermograms. Two TG parameters, the amount of residue produced and the rates of weight loss, offer ways to predict the effectiveness of a PCA with respect to smooth-drying character. The presence of the catalyst influenced both measurements in desirable directions. Finally, the catalyst did not alter TG water loss data that support the proposed mechanism of reaction with cellulose via an anhydride intermediate.

INTRODUCTION

A large variety of chemical agents are capable of producing durable press (DP) properties by cross-linking cotton cellulose. To treat fabric, these agents require the presence of a catalyst and a heat cure to induce crosslinking of cotton cellulose and achieve an acceptable smooth-drying DP finish. The resulting DP properties can disappear over time because some finish bonds with cellulose are reversible. Finish breakdown from current formaldehyde-based agents involves release of formaldehyde.[1] Because formaldehyde has been identified as a probable human carcinogen, attempts have been made at the Southern Regional Research Center to replace the traditional agents with new ones that will cause no release of formaldehyde. In the latest and most successful attempt, polycarboxylic acids (PCAs) were evaluated as durable press agents for cotton. With these agents catalysts from alkali metal salts of inorganic phosphorus acids are co-reactants. Some PCAs were found to perform as well or better than DP finishes on the market today.[2-5]

Concurrently with finish research, a study of the basic properties of these polycarboxylic acids was begun. The thermal characteristics of these PCAs have been reported.[6] Thermoanalytical (TA) and mass spectrometric (MS) studies were performed using two simulated cure conditions where the initial effects of one sodium salt of a phosphorus-containing inorganic acid catalyst were noted.[7] We chose sodium dihydrogen phosphate monohydrate as our catalyst because its use in fabric treatments produced intermediate levels of DP properties, and we needed to learn if our analytical procedures could detect any changes at all. This current research

Table I Pad Solution Concentrations of Polycarboxylic Acids[a]

	Agent (%)[b]
Dicarboxylic Acids	
Maleic	6.4
Succinic	6.4
Tricarboxylic Acids	
Tricarballylic	6.3
Citric	6.9
Tetracarboxylic Acids	
1,2,3,4-Butanetetracarboxylic (BTCA)	6.3
All-cis-cyclopentanetetracarboxylic (CP-TCA)	6.6
Tetrahydrofurantetracarboxylic (THF-TCA)	6.3

[a] The catalyst was 4.2% $NaH_2PO_4H_2O$ in all cases.
[b] Concentrations were adjusted to produce a carboxyl content equivalent to that of BTCA.

concentrates on the effects of the same catalyst on the MS and TA properties of seven PCAs under higher temperature conditions and includes some evidence that the presence of this catalyst does not change the proposed reaction mechanism that involves formation of an anhydride intermediate. In the future, if these catalyst effects can be correlated to textile finishing improvements, we could predict catalyst efficiency without time-consuming textile treatments and fabric testing.

MATERIALS AND METHODS

A series of di-, tri-, and tetra-functional PCAs was examined. Acids were analyzed alone as solids. Acid–catalyst mixtures were tested after their solutions were dried to constant weight in a vacuum oven at 60°C. Only the citric acid–catalyst specimen was not a solid. The acids chosen and the concentrations of acid–catalyst solutions are given in Table I. All chemicals were research grade, commercially available products.

Mass spectrometric analyses were performed by direct probe sample insertion in a Finnigan 4500 mass spectrometer* using electron impact ionization

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* Names of companies or commercial products are given solely to provide scientific information, and their inclusion does not imply endorsement by the U.S. Department of Agriculture over others not mentioned.

(70 eV). Samples were prepared from solutions that were dried directly into a sample vial and were approximately 50 μg each. Ions were collected over the mass range of 30–450 amu at one scan/s. Data were analyzed with the instrument's Incos data system.

Thermoanalytical data were acquired with a DuPont 1090 thermoanalyzer using differential scanning calorimetric (DSC) and thermogravimetric (TG) procedures. DSC samples were normalized to 5.0 mg sample size; TG samples were 10–12 mg. Samples were analyzed under dynamic nitrogen conditions.

In both instruments samples were heated under programmed conditions. All were held at 60°C for 3 min, heated at a rate of 15°C/min to 300°C, then held for 3 min at the maximum temperature.

RESULTS AND DISCUSSION

Mass Spectrometric Results

An initial study of the individual spectra showed no readily apparent differences in ion profiles caused by the presence of the monosodium phosphate catalyst. We did not expect to see ions from the catalyst itself. Our attention focused on the reconstructed ion current (RIC) chromatograms. While not as precise a profile of a compound as a DSC thermogram, RICs do show some compound individuality. The RIC peak represents the production of the greatest abundance of ions and is dependent on agent structure and somewhat upon its thermal characteristics. The peaks occur at various positions (time/temperature). Initial catalyst effects were found in the simulated cure temperature study,[7] where samples were heated at a greater rate to a maximum of 160 or 180°C. Catalyst effects were indicated by shifts in the position of major ion production to lower times and temperatures.

The RICs of the di-functional acids are shown in Figure 1. These acids are of scientific but not textile interest. According to the hypothesis of the way the PCAs crosslink cellulose, which we discuss later, the dicarboxylic acids can react once but not crosslink. Maleic acid, with its unsaturated bond, ionizes very rapidly in the mass spectrometer. In the absence of monosodium phosphate, this acid produced the majority of its ions in two peaks. The first peak (near 50 s) was completed during the initial isothermic period (60°C), and was small. The second peak was smaller (near 250 s), and ion production was complete by 400 s. The presence of catalyst caused ion production to be spread over a greater time and
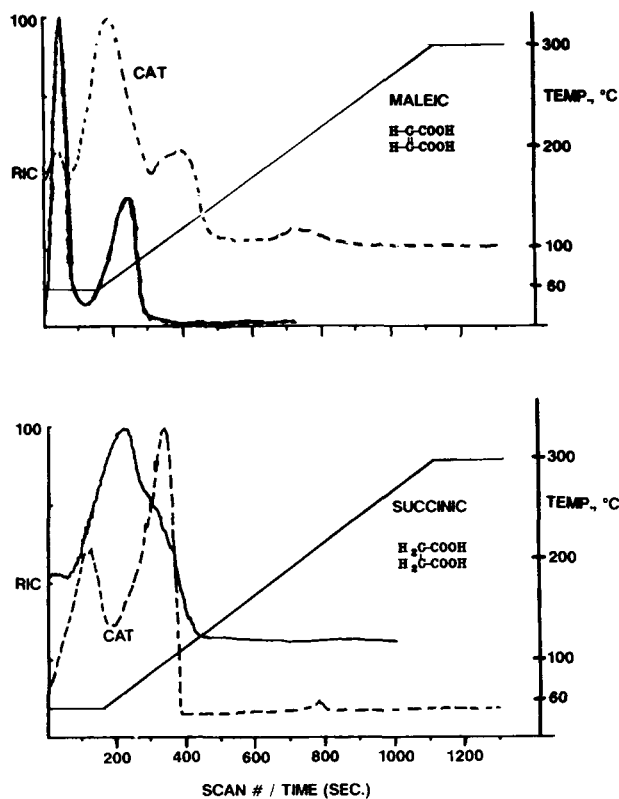
Figure 1 Reconstructed ion current chromatograms (RIC) of dicarboxylic acids alone (solid line) and in the presence of sodium dihydrogen phosphate monohydrate catalyst (dashed line). Temperature gradient shown (y_2 axis).

temperature period. The majority of ions were produced near 200 s.

Succinic acid RIC curves were changed from a single peak with a shoulder to a double peak when catalyst was present. The first peak was near 120 s versus 200 s for acid alone, and ion production ended at about the same time/temperature. Both di-functional acids exhibited the most complicated behavior in the presence of monosodium phosphate. Ion production was the earliest for those acids.

Figure 2 shows the RIC data for the tri-functional acids. These compounds are capable of crosslinking cotton and do produce smooth-drying properties with fabric.[8,9] With these acids we saw the first example of a common effect due to the presence of monosodium phosphate. The presence of the catalyst with tricarballylic acid produced an obvious RIC peak shift to a shorter time and lower temperature.

Citric acid results were similar. In addition, the catalyst caused jagged ion production in the RIC from melting and bubbling. The first large spike was shifted in the same direction.

The results of the three tetra-functional acids are shown in the next two figures. With both cyclic tetracarboxylic acids (Fig. 3), the presence of monosodium phosphate caused shifts similar to those seen with the less substituted acids. Butanetetracarboxylic acid (BTCA, Fig. 4), the first acid showing excellent results on textile substrates among the PCAs, also produced ions at lower temperature/time when in the presence of the catalyst.

Our study at simulated cure conditions[7] as well as this high-temperature study produced similar results. All data showed differences in the RICs when catalyst is present and most showed shifts in ion production to a lower temperature and shorter time.

We used MS RIC data qualitatively. Since the RICs are normalized, the differences between the curves do not necessarily indicate relative ion production. That is, it is the temperature of ion production that is significant and not peak intensity. With TA we have a simpler means of comparison because TG data are reported in percentages and
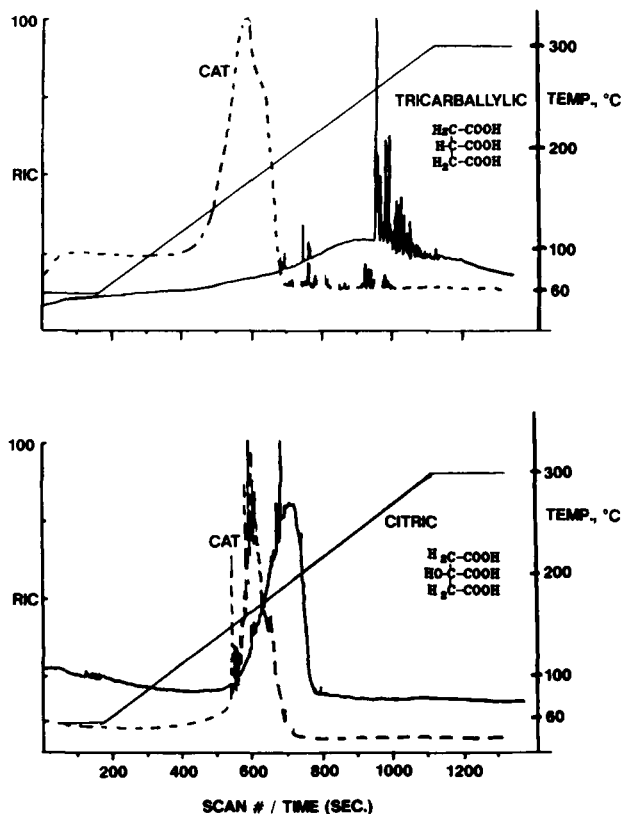

Figure 2 Reconstructed ion current chromatograms (RIC) of tricarboxylic acids alone (solid line) and in the presence of sodium dihydrogen phosphate monohydrate catalyst (dashed line). Temperature gradient shown (y_2 axis).
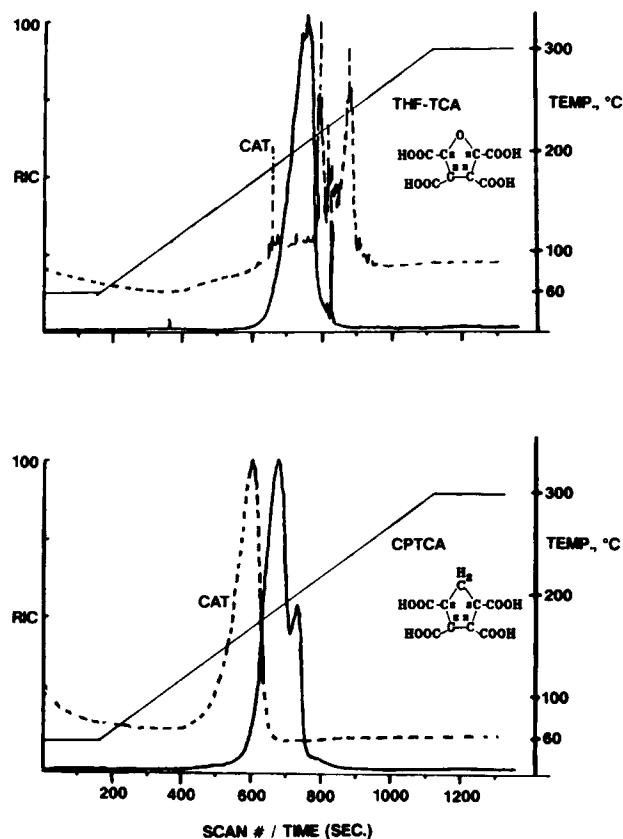
Figure 3 Reconstructed ion current chromatograms (RIC) of cyclic tetracarboxylic acids alone (solid line) and in the presence of sodium dihydrogen phosphate monohydrate catalyst (dashed line). Temperature gradient shown (y_2 axis).
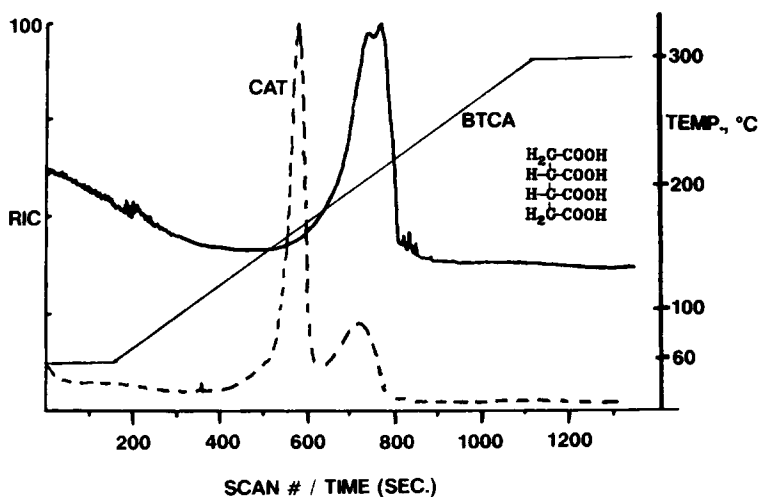
DSC curves can be normalized to a constant sample size so that relative peak intensity is significant.

Thermoanalytical Results

The next figures show the DSC thermograms of the seven PCAs. All DSC peaks in this study are endothermic, i.e., the sample absorbed heat as it was heated. Two curves are shown for each acid—one with and one without monosodium phosphate. Results from analysis of di- and tri-functional acids are given in Figures 5 and 6. In each instance the thermogram of the sample with acid and catalyst was different from the corresponding acid alone. Peak intensities were always diminished and often peaks were positioned at lower times/temperatures.

Similar results were found with the tetra-functional acids shown in Figures 7 and 8. The DSC thermogram for the catalyst itself at a sample size equivalent to its concentration in the mixed samples is also shown (Fig. 8). With catalyst alone only one peak was present (at 14–15 min), and this peak is rarely seen in the DSC curves of an acid–catalyst mixture. The tricarballylic thermogram did contain this peak, however.

With the instrument software one can modify the DSC curves of the acid alone and the catalyst alone so that their sample sizes correspond to those found in the mixture. By adding the two curves representing 3 mg acid and 2 mg catalyst and by comparing the result (not shown) to the corresponding
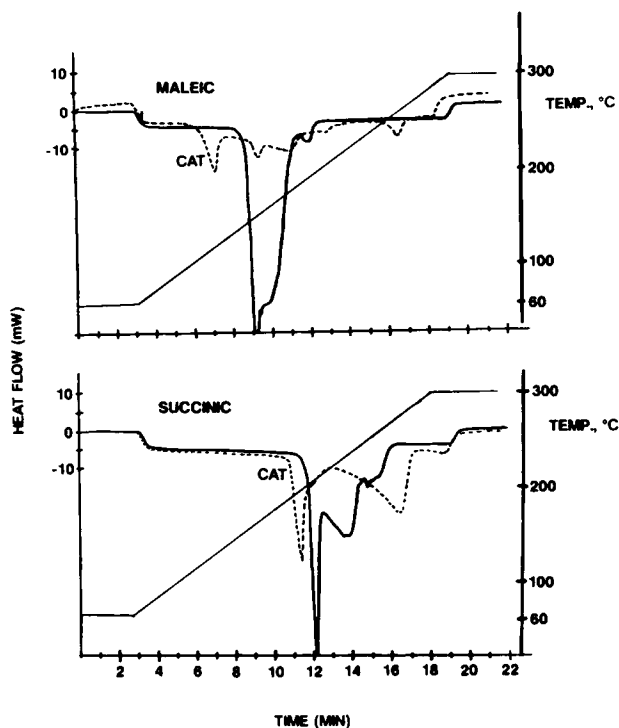

Figure 4 Reconstructed ion current chromatograms (RIC) of 1,2,3,4-butanetetracarboxylic acid alone (solid line) and in the presence of sodium dihydrogen phosphate monohydrate catalyst (dashed line). Temperature gradient shown (y_2 axis).

Figure 5 Differential scanning calorimetric (DSC) thermograms of dicarboxylic acids alone (solid line) and in the presence of sodium dihydrogen phosphate monohydrate catalyst (dashed line). Temperature gradient shown (y_2 axis).

actual thermogram, we found that the thermograms' peak positions and intensities were similar. We concluded that the catalyst effect was generally additive as opposed to synergistic.

The temperature range of DSC thermal activity was the interval that began when the curve left the baseline and ended when the thermogram returned to the baseline. Total heat of reaction in joules per gram for each sample is the integrated area between the curve and the baseline. The total heat values that represent the acids with and without catalyst are given in Figure 9. In all cases these values were diminished in the presence of the catalyst.

Thermogravimetric data were extremely valuable. Our earliest thermal information on the PCAs indicated that the best durable press fabrics were achieved with acids that had low rates of weight loss.[6] We averaged the maximum rate of weight loss data, with and without monosodium phosphate present, and plotted these data for all the acids in Figure 10. The presence of catalyst decreased the rates of weight loss for all the PCAs and should improve the DP performance of all the acids.

Both di-carboxylic acids and citric acid had the highest rates of weight loss without catalyst. With catalyst, maleic acid had the greatest change in rate of these three acids. Of the cyclic acids, CP-TCA had the lower rate of weight loss. In fact, THF-TCA was affected the least of all acids studied. Were it not for cost, CP-TCA would be among the acids of highest interest.

Those that are of most interest to the textile industry are tricarballylic, BTCA, and citric. Citric acid continues to be examined because it is commercially produced already and is nontoxic. Using rates of weight loss data as a predictor of good smooth-drying performance in textiles, we would rank these three acids: tricarballylic > BTCA > citric.

Another piece of TG data that was found useful in predicting fabric performance was the amount of residue at the end of the analysis. Our early work indicated that better performance was achieved with acids that left high residues.[6] The residue data are plotted with and without catalyst present in Figure 11. In all instances the presence of monosodium phosphate increased the amount of residue remain-
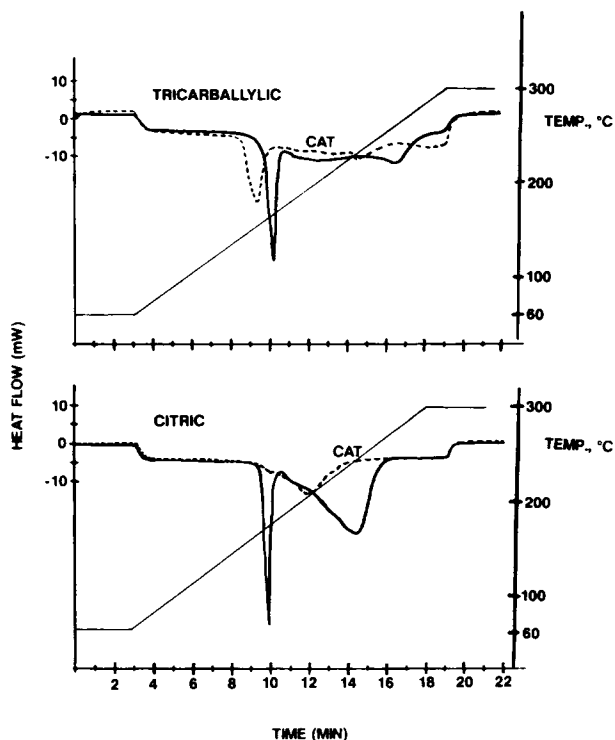

Figure 6 Differential scanning calorimetric (DSC) thermograms of tricarboxylic acids alone (solid line) and in the presence of sodium dihydrogen phosphate monohydrate catalyst (dashed line). Temperature gradient shown (y_2 axis).
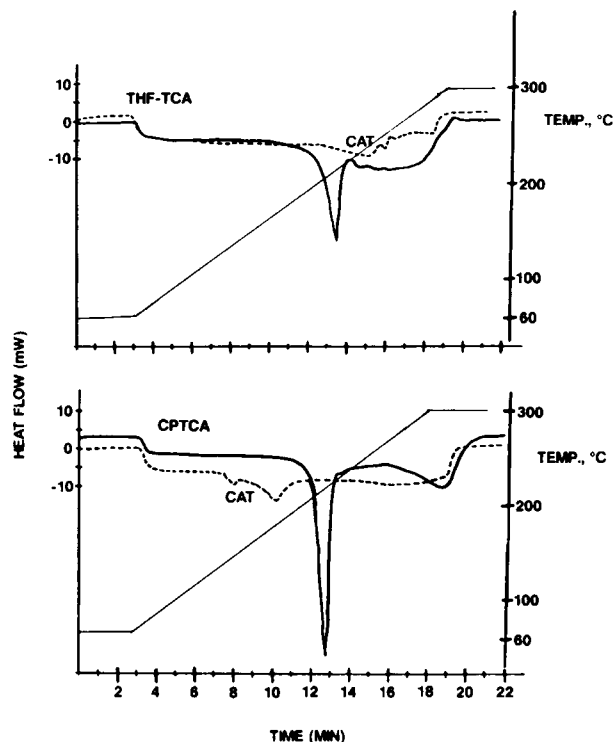
Figure 7 Differential scanning calorimetric (DSC) thermograms of cyclic tetracarboxylic acids alone (solid line) and in the presence of sodium dihydrogen phosphate monohydrate catalyst (dashed line). Temperature gradient shown (y_2 axis).
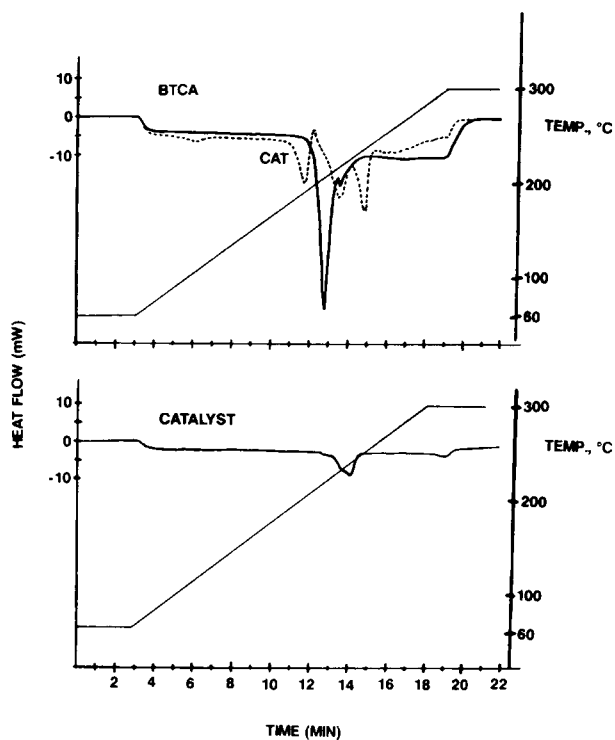
Figure 8 Differential scanning calorimetric (DSC) thermograms of 1,2,3,4-butanetetracarboxylic acid alone (solid line) and in the presence of sodium dihydrogen phosphate monohydrate catalyst (dashed line). DSC thermogram of catalyst alone at the concentration found in acid–catalyst mixtures. Temperature gradient shown (y_2 axis).

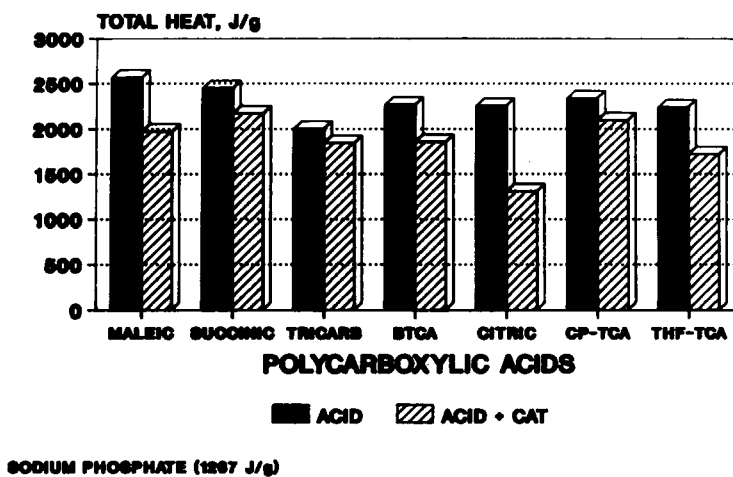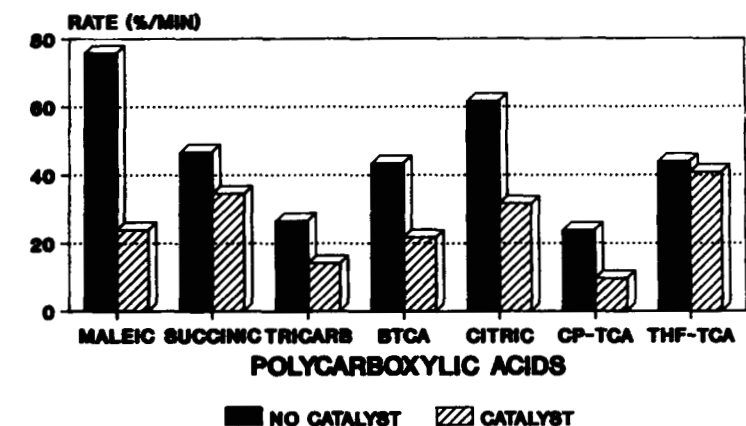# EFFECT OF CATALYST
TOTAL HEATS of REACTION

Figure 9 The effect of sodium phosphate catalyst on total heats of reaction (joules/gram) of polycarboxylic acids—from differential scanning calorimetric (DSC) thermograms.
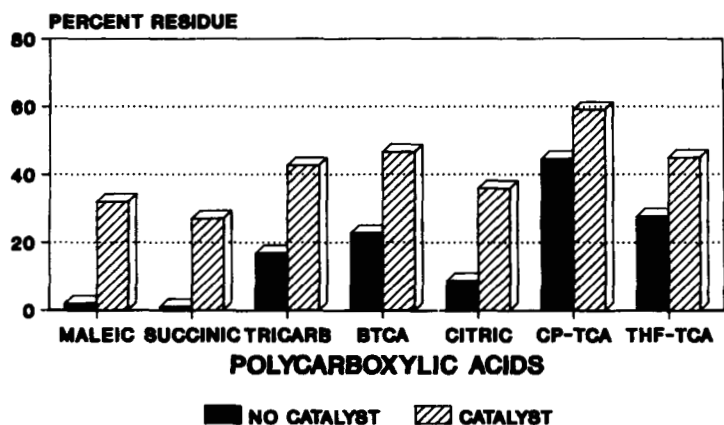
EFFECT OF CATALYST
RATE OF WEIGHT-LOSS

Figure 10   The effect of sodium phosphate catalyst on rates of weight loss data (% weight loss/min) of polycarboxylic acids—from differential thermogravimetric (DTG) thermograms.

ing at the end of the run. The effect is most often simply additive with respect to residue (i.e., we could predict the amount of residue by adding 60% of residue produced by the acid alone to 40% of residue produced by this catalyst alone).

The residue production of di-functional acids was

improved but was still the lowest among the acids studied. CP-TCA again showed better results than the other cyclic compound. Actually, CP-TCA gave the best results of all the acids when low rates of weight loss and high residue data were the criteria. Of the three acids with the most current textile in-

EFFECT OF CATALYST
PERCENT RESIDUE

Figure 11   The effect of sodium phosphate catalyst on percent residue data (% weight loss) of polycarboxylic acids—from differential thermogravimetric (DTG) thermograms.

terest, residue data can be used to rank them with or without catalyst as follows: BTCA > tricarballylic > citric.

Of the two analytical methods we have examined, TA appears to be the most versatile. It offers a variety of parameters that can be measured easily and a means to make quantitative comparisons among the PCAs possible.

Reaction Mechanism

While conventional DP reactants crosslink with cellulose through etherification, reaction of PCAs with cellulose occurs through an esterification process.[4] PCAs are believed to form a cyclic anhydride intermediate that then reacts with a hydroxyl group on the cellulose molecule forming an ester linkage and regenerating a free carboxylic acid group. We believe that crosslinking reactions are only possible by an anhydride mechanism with a carboxylic acid
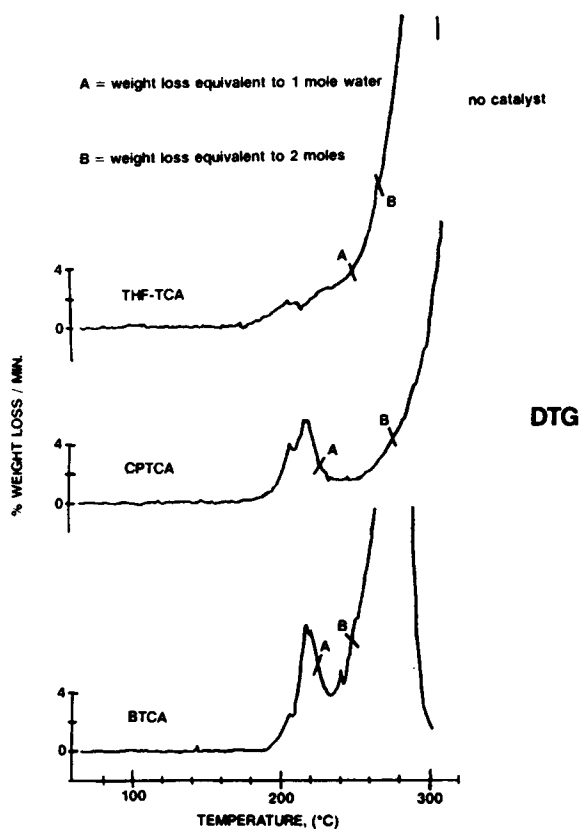

Figure 12 Differential thermogravimetric curves for tetracarboxylic acids shown. Regions of weight loss highlighted represent proposed water loss. BTCA = 1,2,3,4-butanetetracarboxylic acid; CP-TCA = all-cis-cyclopentanetetracarboxylic acid; THF-TCA = tetrahydrofuran-tetracarboxylic acid.

Table II Percent Weight Loss of Tetracarboxylic Acids in DTG

Acid	A calc[a]	A (Fig.)	B calc[b]	B (Fig.)
THF-TCA	11.31	11.40	6.96	7.01
CP-TCA	11.38	11.37	6.99	6.61
BTCA	11.83	11.57	7.21	7.47

[a] Weight loss equivalent to 1 mol water from acid plus 0.5 mol water from catalyst (adjusted for 60% acid + 40% catalyst).

[b] Weight loss equivalent to 2 mol water from acid plus 0.5 mol water from catalyst (adjusted for 60% acid + 40% catalyst).

having three or more functional groups so that a second anhydride moiety could form and react with cellulose. Theoretically, a tetracarboxylic acid has the potential to form a dianhydride in one step.

The results of both MS and TA techniques[6,7] run on the acids in the absence of catalyst provided evidence that water loss (anhydride formation) occurs upon heating the PCAs. The best evidence in MS data was found with the specific ion current chromatograms of the water ion, and ancillary evidence was found in the large number of ion fragments with plausible anhydride structures.

The best TA evidence was found when the tetracarboxylic acids were heated to 600°C.[7] Similar results were found when the acids were heated to 300°C in the present study. Using the data from the three tetracarboxylic acids, we expanded the temperature scale of the differential thermogravimetric (DTG) curves to search for early changes in the rate of weight loss that might represent the loss of water. Comparisons of the theoretical weight loss of 1 mol of water and the actual weight losses were made, and good agreement was found. Furthermore, evidence for the loss of 2 mol of water was found with CP-TCA and BTCA, and not found with THF-TCA (Fig. 12). With THF-TCA the position on the DTG curve that represented a second mole of water loss was considered too high up the steepest weight loss peak. We believe that the relative positions of the carboxylic acid groups in the THF-TCA molecule are not such that a dianhydride could form. However, the all-cis structure of CP-TCA made dianhydride formation possible. The linear BTCA molecule had the freedom to rotate, and this made dianhydride formation with this acid possible. BTCA data provided the best evidence of the loss of 2 mol of water.

When the catalyst was present with each acid, we calculated the theoretical weight loss equivalent to loss of 1 or 2 mol of water from each sample. These data were corrected for reduced acid concen-

tration in the mixture plus the weight of 0.5 mol of water lost by the sodium dihydrogen monohydrate portion. The theoretical and actual data from the expanded DTG curves are shown in the Table II for comparison. The agreement was excellent. The actual data are given on the DTG curves in Figure 13.

Once again the CP-TCA and BTCA offered evidence for loss of a second mole of water and therefore the best possibility of formation of a dianhydride. Clearly the BTCA data were again best. The formation of a dianhydride intermediate should simplify crosslinking with cotton by these agents. These new DTG data offer additional support for the proposed mechanism for the reaction of the PCAs with cellulose.

SUMMARY AND CONCLUSIONS

Using mass spectrometric and thermoanalytical techniques we have examined the effects of the catalyst sodium dihydrogen phosphate monohydrate on seven polycarboxylic acids that are under investigation as durable press reactants for cotton. Using MS, we recognized that the presence of monosodium phosphate caused the reconstructed ion current chromatograms of the PCAs to change. In most instances ion fragmentation began at an earlier time and lower temperature. This indicated that catalyzed reactions might begin quicker and use less energy.

DSC tests showed that, when catalyst was present, peak intensities were always diminished and thermal activity often occurred at lower temperatures/earlier times. These data are consistent with the MS results. The TG data were the most useful, and were easy to obtain. Early research indicated that high residue production and a low maximum rate of weight loss by the acids were good predictors of fabric DP results. In the present study the use of a catalyst gave even higher residues and lower rates of weight loss with all of the PCAs tested. With residue production in particular, the catalyst effect was generally additive.

In search of support for anhydride-intermediate formation as the reaction mechanism for cellulose esterification, the DTG curves of acids plus catalyst showed evidence of significant water loss (and therefore anhydride formation) with the tetra-functional acids that most easily crosslink cotton cellulose. The strongest indirect evidence of dianhydride formation was found with BTCA, the agent showing the most promise and causing the greatest interest in the textile industry.
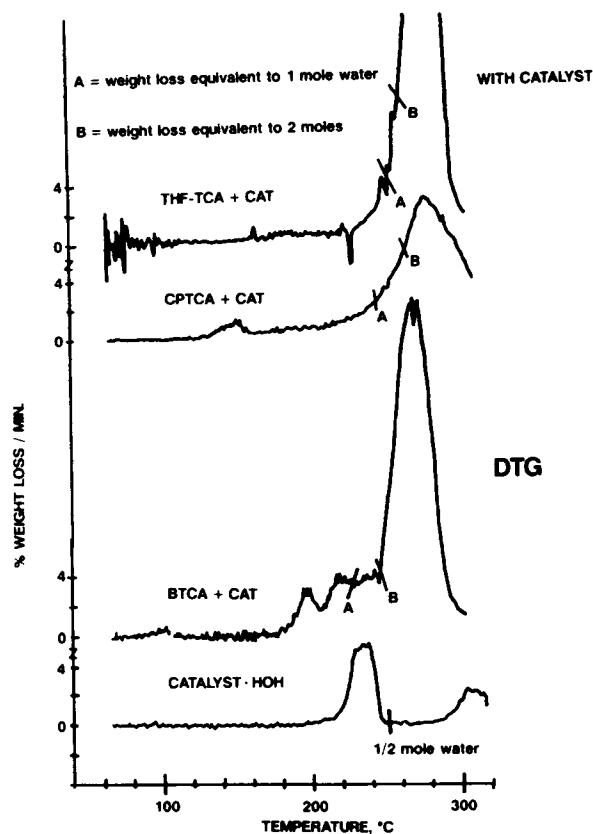

Figure 13 Differential thermogravimetric curves for tetracarboxylic acids shown and sodium phosphate catalyst. Regions of weight loss highlighted represent proposed water loss corrected for concentrations in mixtures and contribution from catalyst itself. BTCA = 1,2,3,4-butanetetracarboxylic acid; CP-TCA = all-cis-cyclopentanetetracarboxylic acid; THF-TCA = tetrahydrofurantetracarboxylic acid.

These test results can be used by textile fabric researchers to shorten developmental research time by eliminating from fabric trials those acids that show the least promise in these model experiments. The catalyst chosen (sodium dihydrogen phosphate monohydrate) was effective but not the best in order to be certain that differences due to catalyst presence were measurable. In the next phase, when these data are combined with results from other catalysts, we should be able to measure differences among catalysts and to predict which catalyst in general would be better with PCAs and perhaps which catalyst in particular should be used with each acid.

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