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B.F. Goodrich Chemical Company
A DIVISION OF THE B.F. GOODRICH COMPANY

RESEARCH AND DEVELOPMENT REPORT

Improved Estol B/1,4 Butanediol Blend Thermal Stability

I. Effect of Stabilizers (Chelators) and
Alternative Polyesterification Catalyst
(Stannous Chloride).

by

K. Dinbergs

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Improved Estol B/1,4 Butanediol Blend Thermal Stability

I. Effect of Stabilisers (Chelators) and
Alternative Polyesterification Catalyst
(Stannous Chloride)

by

K. Dinbergs

SUMMARY & CONCLUSIONS

Estol B [poly(tetramethylene adipate)glycol] and 1,4 BDO (1,4-butanediol) are blended in precise molar ratios for use in Estane manufacture. The ratio of these two components, as well as the molecular weight of the Estol B, determines Estane composition, properties, and performance and is, therefore, critical. Over a period of time some serious problems were encountered in the performance of certain commercial Estanes, including polymers sold for adhesive applications (5713), and more recently, automotive injection molding applications (58130).

The above problems were felt to be related to the reduction of Estol B molecular weight in the blends by thermally induced alcoholysis of the polyester via the 1,4 BDO chain extender component during the makeup, storage, and use of the blends in the Estane manufacturing process. Such alcoholysis reduces the molecular weight of the Estol B (polyester) component, and simultaneously consumes free 1,4 BDO by incorporating it in the shortened polyester chains. This change assures that the contemplated Estane product will not be obtained on subsequent Estane polymerization with MDI (diphenylmethane-p,p'-diisocyanate). The growing seriousness of the blend alcoholysis problem led to a major effort to find a satisfactory solution. Research joined Production and Development in this effort in March, 1974.

My study of the problem, using gel permeation chromatography (GPC) and gas chromatography (GC) as tools, has shown that the thermally induced alcoholysis of Estol B-1,4 BDO blends is strongly accelerated by the titanium, residual from the Production Estol B polyesterification catalyst, tetra (2-ethylhexyl) titanate (TEHT). And that this alcoholysis increases with increasing blend temperature, 1,4 BDO concentration, and TEHT concentration.

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In the course of my studies I investigated two routes to more stable Estol B/1,4 BDO blends. These were: (1) the use of small amounts of chelating agents for titanium in blends containing TEHT catalyzed Estol B; (2) the use of an Estol B polyesterification catalyst alternative to TEHT which does not accelerate polyester alcoholysis in the blend. Both approaches have proved to be fruitful.

Chelators - Effective and adequate chelators found include quinolinol (Q) and acetylacetone (AcAc). However, Q has a persistent medicinal odor and AcAc has some odor. Ethylenediamine tetraacetic acid (EDTA), which is odorless, should be an effective chelator for titanium but it is ineffective, most likely due to its insolubility in the blend. Moreover, it contains hydrolysis accelerating carboxyl groups. So I prepared N,N,N',N'-tetra-n-butyl ethylenediamine tetraacetate (TB EDTA) which proves to be a colorless, essentially odorless, soluble, high boiling liquid. Moreover, tests show that even at low levels TB EDTA is a good, possibly adequate, stabilizer of Estol B-1,4 BDO blends against thermally induced, TEHT-accelerated alcoholysis, presumably by its unexpectedly good ability to chelate titanium.

The above chelators are quite effective in stabilizing TEHT-containing blends at ~0.2 parts per hundred of blend (wt.). And neither Q nor AcAc at these levels adversely affect the measured original properties/environmental stability of the Estane tested (5701). The effect of TB EDTA on Estane environmental stability has not been determined.

Alternative Catalysts - I found that Estol B/1,4 BDO blends made from Estol B whose formation was accelerated by the alternative polyesterification catalyst, stannous chloride dihydrate ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$), show remarkable and adequate inherent stability to alcoholysis at typical temperatures encountered in blend makeup, storage, and use. And that at (effective) levels of ~65 ppm, $\text{SnCl}_2 \cdot \text{H}_2\text{O}$ catalyst/residue does not significantly affect the measured original properties/environmental resistance of Estane 5701, with the exception that long term heat aging (140°C./air) and stress-strain properties are slightly poorer.

In the course of the present investigation I made two other interesting and worthwhile discoveries, namely: (1) treatment of 1,4 BDO with 4A molecular sieves at ~90°C. produces tetrahydrofuran, apparently by a cyclodehydration reaction, in good yield; (2) contamination of Estane with imperceptible PVC dust by routine mill-massing the Estane on our "clean" plastics mill has, for some time, introduced invisible PVC particles into the Estane. These particles become brown specks when the Estane is heat aged (140°C.) in air which intensify with aging time, apparently evolving an agent (HCl ?) which diffuses radially into the surrounding Estane matrix, turning it yellow and eventually brown.

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The foregoing results of my investigation, which were confirmed by ALTC studies, allowed a choice - chelation or alternative Estol catalyst - to be made in solving the blend stability problem. Supported by the valuable guidance of Dr. L. E. Hewitt's thermal analysis studies and ALTC molding trials and property evaluations, the latter option was selected to meet the urgent Estane 58130 injection molding polymer problem. It was promptly applied by Production in timely rescue of that promising automotive business.

OBJECTIVES

The objectives of this study were to determine the basic cause of Estol B/1,4 BDO blend instability and then provide means of overcoming the problem that would be acceptable and adaptable to our Estane manufacturing process.

RECOMMENDATIONS

In order to produce Estol B-1,4 BDO blends of adequate thermal stability for use in manufacturing Estane thermoplastic polyurethanes, I recommend that minimum effective levels of stannous chloride dihydrate be substituted for tetra (2-ethylhexyl) titanate (TEHT) as Estol B polyesterification catalyst. Or in the event that the use of TEHT as Estol B polyesterification catalyst be continued, I recommend that one of the following metal chelators be considered as an additive to blends which contain TEHT-catalyzed Estol B in order to stabilize the blends against thermally induced polyester alcoholysis: acetyl acetone (AcAc); N,N,N',N'-tetra-n-butyl ethylenediaminetetraacetate (TB EDTA); or 8-hydroxyquinoline (quinolinol, Q). If the persistent medicinal odor of Q can be tolerated.

Should interest warrant, the preparation of tetrahydrofuran by the cyclo-dehydration of 1,4-butanediol via molecular sieves should be further studied.

The adverse effect of PVC on Estane color when such combinations are heated should be borne in mind in deciding their applications.

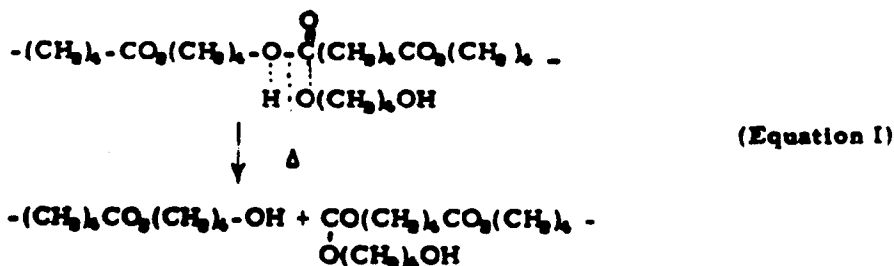
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To produce low acid number Estol B [poly (tetramethylene adipate)] glycol Estane Production has catalysed the polyesterification reaction with tetra (2-ethylhexyl) titanate (TEHT) using levels ranging from 15 to about 10 ppm. This Estol B is then blended with various amounts of 1,4-butanediol and stored for about 10-14 days (but occasionally up to one month) at elevated temperatures awaiting use in the Estane manufacturing process. Storage temperature depends on the type of blend used. It can range from 140°F. (60°C.) to 200°F. (93°C.), and for high molecular weight Estol B (> 3000 MW) it could exceed 200°F.

In the case of Estol B/1,4 BDO blend alcoholysis the 1,4-BDO leaves the polyester chain and combines with the broken chain fragment that carries the carboxy fragment, thus reducing the average molecular weight of the polyester component and consuming free 1,4 BDO. But "blend molecular weight" remains unchanged. This reaction is illustrated in Equation I.



In my earlier study (1) I found that this alcoholysis reaction is accelerated by heat, high 1,4-BDO concentration, and catalysts. I also found the rate of alcoholysis of uncatalyzed blends to be quite slow at ~100°C. But at 140°C. noticeable alcoholysis occurred, and at 170°C. the alcoholysis rate was fairly rapid!

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In addition, I found that under the same conditions an uncatalyzed blend containing 2 moles of 1,4-BDO underwent noticeable alcoholysis, whereas a blend containing only 1 mole of 1,4-BDO did not. Furthermore, I found that the phenolic antioxidant, CAO-1[2,6-di-tertiary butyl-p-cresol] is a catalyst for the alcoholysis reaction in Estol B-1,4-BDO blends.

My earlier report (1) concludes that uncatalyzed Estol B (M. W. 1000) 1,4-BDO blends containing 0.3 or 1.0 mole of 1,4-BDO cannot be heated for >24 hours at about 100°C., and blends containing 2.0 moles 1,4-BDO cannot be heated at >50°C. without measurable alcoholysis of the Estol B.

The objectives of the work described in my present report were to pinpoint the basic cause of the severe alcoholysis problem currently encountered in Estol B/1,4-BDO blends and to determine how to provide Production with a route to more alcoholysis-stable blends for Estane manufacture. I have found that this can be accomplished by using an effective stabilizer (metal chelator) in the blends or by the use of an alternative Estol B polyesterification catalyst that does not subsequently catalyze blend alcoholysis and does not significantly affect the environmental resistance of the derived Estane (3A). The effectiveness of the stabilizers and the alternate catalyst was confirmed at Avon Lake (3B, C, D, E, F, G).

Experimental Part

I Materials

1. Estol B [poly (tetramethylene adipate)glycol]. The following Estol B lots were used in this study:

- (A) 7745-74-5, Estol 5711, Tank #5, BLD #608 and #609, Avon Lake anal. OH# 54.58, Acid #0.31, Mol. Wt. 2032. Brecksville anal. OH# 54.2, Acid # 0.4, Mol. Wt. 2040. Contains 3.5 ppm tetra (2-ethyl hexyl) titanate according to X-ray fluorescence analysis.
- (B) 2074-70-1150B, OH# 56.7, Acid #0.1, Mol. Wt. 1972 made with 67 ppm $\text{SnCl}_4 \cdot 2\text{H}_2\text{O}$ calculated at the point of addition (after the removal of water but before transesterification), water washed. Calculated amount of tin in the polyester, 49 ppm. Calculated amount of tin in the blend with 2.00 moles 1,4-butane-diol, 45 ppm. Tin found by X-ray fluorescence in the blend made from water extracted Estol B, 42 ppm (93% of the calculated amount).
- (C) 2074-72-2468, OH# 50.7, Acid # 0.2, Mol. Wt. 2192. Made with 75 ppm $\text{SnCl}_4 \cdot 2\text{H}_2\text{O}$ calculated at the point of addition (after removal of water but before transesterification). Water washed.

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- (D) 7745-75-72, OH# 68.4, Acid #0.2, Mol. Wt. 1631. Made with 65 ppm $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ calculated on the weight of the polyester after the removal of water but before transesterification. Not water washed.
- (E) 5740-73-231, OH# 94.4, Acid #0.2, Mol. Wt. 1184. Made with $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ catalyst; amount at the point of addition (after the removal of water but before transesterification), 75 ppm. Amount calculated on the final polyester, 98 ppm. Water washed. Contains 199 ppm water.
- (F) 7742-75-181, OH# 131.2, Acid #0.5, Mol. Wt. 849. Made at Avon Lake with 10 ppm TEHT catalyst, not water washed, contains 1.95% free 1,4-butanediol, background molecular weight 1020, contains 284 ppm water.
- (G) 5740-73-335, OH# 113.0, Acid #0.3, Mol. Wt. 988. Made with 76 ppm stannous chloride dihydrate catalyst at the point of addition (after the removal of water but before transesterification). Theoretical amount of tin in the final polyester, 52 ppm.

2. 1,4-Butanediol

- (A) 7745-74-5. Production material obtained from Avon Lake. Contains 2461 ppm water.
- (B) 7741-74-410, anhydrous, Akron Chemical Company (Antara - General Aniline and Film Co.) It was purified by vacuum distillation, b.p. 122-126°C/8-9 mm, contains 116 ppm water.
- (C) 7741-74-23, anhydrous, Akron Chemical Company (Antara - General Aniline and Film Co.). It was purified by vacuum distillation, b.p. 118-123°C. at 8-10 mm, contains 92 ppm water.
- (D) 7742-75-189, Received from Avon Lake, BASF, contains 1967 ppm water.

3. Estol B/1,4-BDO Blend

ALGCP #855, Brecksville #7745-76-173A, M.W. 545, A.N. 0.6, 311 ppm water, was made with 10 ppm of TEHT catalyst but according to analysis by X-ray fluorescence contains 6.7 ppm TEHT.

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4. MDI (p,p'-Diphenylmethane diisocyanate)

- (A) 5740-73-549, Mobay Multirathane M, flaked. 99.2% pure, 8 ppm hydrolyzable chloride, was used without purification but corrected for purity.
 - (B) 7742-75-182, Upjohn, 99.3% pure, 28 ppm hydrolyzable chloride, was used without purification but corrected for purity.
 - (C) 7741-74-278A, Mobay Multirathane M, flaked. 99.4% pure, 8 ppm hydrolyzable chloride, was used without purification but corrected for purity.
 - (D) 5740-73-530, Mobay Multirathane M, flaked. 99.6% pure, 6 ppm hydrolyzable chloride was used without purification but corrected for purity.
 - (E) 7741-74-411, Mobay Multirathane M, flaked, 99.2% pure, 12 ppm hydrolyzable chloride, was used without purification but corrected for purity.
 - (F) 7745-76-173C, Upjohn, 99.3% pure, 6 ppm hydrolyzable chloride.
- 5. Tetra (2-ethyl hexyl) titanate (TEHT) obtained from Avon Lake, manufactured by the Stauffer Chemical Co.
 - 6. Stannous Chloride Dihydrate, B&A, General Chemical Division, Allied Chemical & Dye Corp., Code 2341.
 - 7. 8-Quinolinel (8-Hydroxyquinoline), Fisher Scientific Company, 0-261, 77885, Lot 723347.
 - 8. Acetyl Acetone (2,4-Pentanedione), Fisher Scientific Company, A-25, Lot 705384.
 - 9. EDTA (Ethylenediamine tetra acetic acid), Tetrine acid, Glyco Products.
 - 10. TBEDTA (N,N,N',N'-tetra-n-butyl ethylenediaminetetraacetate) prepared in our laboratory (7745-75-148). Acid #: original 0.8, after 1 year's storage 7.6.
 - 11. Tannin (Tannic Acid), Fisher Scientific Company, A-308.
 - 12. 4,4,4-Trifluoro-1-(2-thienyl)-1,3-butanedione, Eastman 7260.

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13. 2,2'-Bipyridine, G. Frederick Smith Chem. Co., Columbus, Ohio.
14. 1,2-Dimethoxyethane, Eastman 1088.
15. Inhibitor NPH (ammonium salt of N-nitrosophenyl hydroxylamine), Mallinckrodt Chemical Works.

II Procedure

1. Heat Aging of Blends

The Estol B was melted and heated to about 50-70°C, then it was blended with the required amount of 1,4-butanediol, and if desired the calculated amount of titanate catalyst was added. Then 150g of the blend was poured into several 8 oz. narrow mouth screw cap bottles, some of which contained various amounts of stabilizers. The stabilizers were dissolved in the blend by shaking, rolling, and occasional heating to temperatures not exceeding 70°C. Most of the stabilizers dissolved very rapidly, some dissolved only partially, but in any case the attempts to dissolve and mix the stabilizers with the blend did not exceed one hour.

After the stabilizers had dissolved in the blend, the original sample was taken by pouring about 20g of the blend into a 1 oz. jar. The bottles containing the blends were then placed in an oven of 93° or at 100°C, and aged for 4 weeks. Samples for analyses were poured from these bottles after each week of aging. During the aging period the caps of the bottles were closed; there was no pressure in the bottles.

2. Preparation of Estane 5701

A. In Glass Beaker - Estane 5701 samples with or without additives or catalyst were prepared by the random melt polymerization technique. 150g of predried Estol B was weighed out in a 400 ml beaker. A 1-7/8" diameter stainless steel propeller type stirrer was inserted in the Estol B and the beaker was placed on a hot plate. With moderate stirring the temperature of the Estol B is raised to 160°C; during this time the additives or catalyst are added. At 160°C, the 1,4 BDO is added from a 20 ml hypodermic syringe. This lowers the temperature of the blend in the beaker to about 150°C. Then, within one minute after the addition of 1,4-butanediol, melted MDI at 140°C, is added from a tared 150 ml beaker. The stirring speed is gradually increased and the reaction mixture is stirred, if possible, for 2 min. In polymerisations containing catalyst, stirring time was reduced to about one-half minute due to the rapid thickening of the polymerization mixture.

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B. In the Brabender Plasticorder Reactor (BPR) - To determine the effect of additives on the polymerization rate, the polymerizations were carried out in the BPR. The apparatus and the polymerisation procedure have been described in an earlier report (4).

III Test Methods

1. 1,4-Butanediol Determination in Estol B/1,4-Butanediol Blends by Gas Chromatography

The gas chromatographic determinations of 1,4-butanediol were carried out by Ilmari Sockis (D/8510) using the Hewlett-Packard 5750 gas chromatograph equipped with thermal conductivity detector. The 1/8" x 2' column contained 10% FFAP on Chromosorb W, 60/80 mesh. Column temp. 150°C. Isothermal, detector temp. 280°C, injection port temp. 260°C. 30 cc/min. helium flow.

To 1-2g of the sample 0.1g of ethylene glycol was added as internal standard, and 10 ml of acetone. The response factor was calculated from a standard solution containing 0.1g of ethylene glycol and 0.1g of 1,4-butanediol dissolved in 10 ml of acetone. All injections were 5.0µl.

2. GPC Analysis of Estol B/1,4-Butanediol Blends

GPC data were obtained by D. J. Harmon (D/8510) with a gel permeation chromatograph, Model 100 (Waters Associates) which had been converted at Breckville to be equivalent to Model 200.

The determinations were made at 40°C. dissolving 40 mg of the blend in 20 ml THF. The solutions were filtered through a syringe filter before injection into the instrument. The syringe filter - Versapor 6429 made by Gelman - has a pore size of 0.90µ, is 13 mm dia., and about 20 mils thick.

It is emphasized that the term and numerical values of "blend $\bar{M}_w$ " (weight average molecular weight) frequently presented in this report are not actually molecular weight values but represent the average molecular size in Angstrom units of the various Estol B/1,4-BDO blends which, of course, contain considerable free 1,4-BDO. And any changes in this $\bar{M}_w$, although due to changes in polyester molecular weight (since $\bar{M}_w$ is primarily affected by the higher molecular weight species of the blend) really represent changes in the $\bar{M}_w$ (average molecular size) of the blend.

However, by inspecting the actual GPC curves, which are also presented in this report, one can readily see the constancy or changes in the molecular weight distribution of the polyester component.

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3. Stress-Strain Properties

For stress-strain tests 6 x 6 x 0.075" or 6 x 6 x 0.025" sheets of the polymers were compression molded for 5 minutes at 180°C. between sheets of Teflon-coated aluminum foil. The tests were run on the Instron Tester (equipped with a pogo) on three 1/8" dumbbells at an elongation rate of 20"/min. All of the samples were conditioned for 24 hrs. at 25°C. and 50% R.H. prior to test.

4. Aging Conditions A

For oven aging 0.075" thick 1/8" dumbbells were aged in a 140°C. forced air oven flat on Teflon.

Hydrolysis resistance was determined by immersing 0.025" thick 1/8" dumbbells in 70°C. water. After removal from water, the samples were desiccated for 24 hours.

Dry Carbon arc Weatherometer aging was carried out on 0.025" thick 1/8" dumbbells.

All aged samples were conditioned for 24 hours at 25°C. and 50% R.H. before testing.

Discussion of Results

I Tetra (2-Ethyl Hexyl) Titanate (TEHT)-Containing Blends

1. Factors that Affect Blend Stability on Heat Aging

A. Temperature Effect on Blend 1,4 Butanediol Content (by Gas Chromatography)

Estol B/1,4-BDO blend aging experiments at Avon Lake carried out by J. Holloway (3C) have shown that the alcoholysis reaction of the polyester is reduced considerably by reducing the blend storage temperature from 93°C. to 70°C. An Estol 5711 blend containing 16% 1,4-BDO and 3.5 ppm titanate catalyst has retained 94% of its original 1,4-BDO content after 4 weeks at 70°C. but only 64% of the original 1,4-BDO content after 4 weeks at 93°C.

Increasing the aging temperature from 93°C. to 100°C. had no significant effect on the alcoholysis reaction.

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B. 1,4-Butanediol Concentration Effect on Blend Molecular Weight Distribution (by Gel Permeation Chromatography)

Another factor that affects the alcoholysis of the polyester is the amount of glycol present in the blend, and I found that the alcoholysis increases with increasing glycol concentration. For example, a blend made from Estol B, M. W. 2032, containing 0.6 moles of added free 1,4-BDO and 22 ppm of TEHT was aged for 4 weeks at 93°C. During this period blend $\bar{M}_w$ decreased from 169.8Å to 143.8Å, a 15% drop.

Another blend made from the same polyester, but containing 2.0 moles of added free 1,4-BDO and 19 ppm TEHT catalyst, decreased in $\bar{M}_w$ from 158.5Å to 104.6Å (a 34% drop) during the same heating period.

Full, normalized GPC curves for the above two blends, before and after heat aging, are shown in Figure 1 (A&B). The molecular weight parameter in these GPC curves is expressed in the abscissa as log Angstrom length of fully extended polymer chains. We can see that the polyester in (B) (blend contains 2.0 moles of 1,4-BDO) has undergone greater changes on heat aging than the polyester in (A) (blend contains only 0.60 moles of 1,4-BDO).

One change that we observe on heat aging is the shift of the major peak to lower molecular weight, with an increase in intensity which must mean that a narrower molecular weight range of reduced polyester chains has resulted. We also see an increase in peaks 2 and 3 counting from the right. These peaks represent lower molecular weight polyester oligomers.

The last peak counting from the right is 1,4-BDO. We can see that the 1,4-BDO peak is greater in (B) than in (A), as expected. On heat aging, the 1,4-BDO peak for both blends decreases indicating that it is consumed by the alcoholysis reaction (Equation I).

C. Catalyst (TEHT) Level - Effect on Blend Molecular Weight Distribution (by Gel Permeation Chromatography)

I also found that the level of TEHT catalyst has a measurable effect on the extent of the alcoholysis reaction. The data on the catalyst level were obtained on a blend containing only 0.60 moles of added 1,4-BDO and, therefore, the changes on heat aging were relatively small. But still, an effect can be seen.

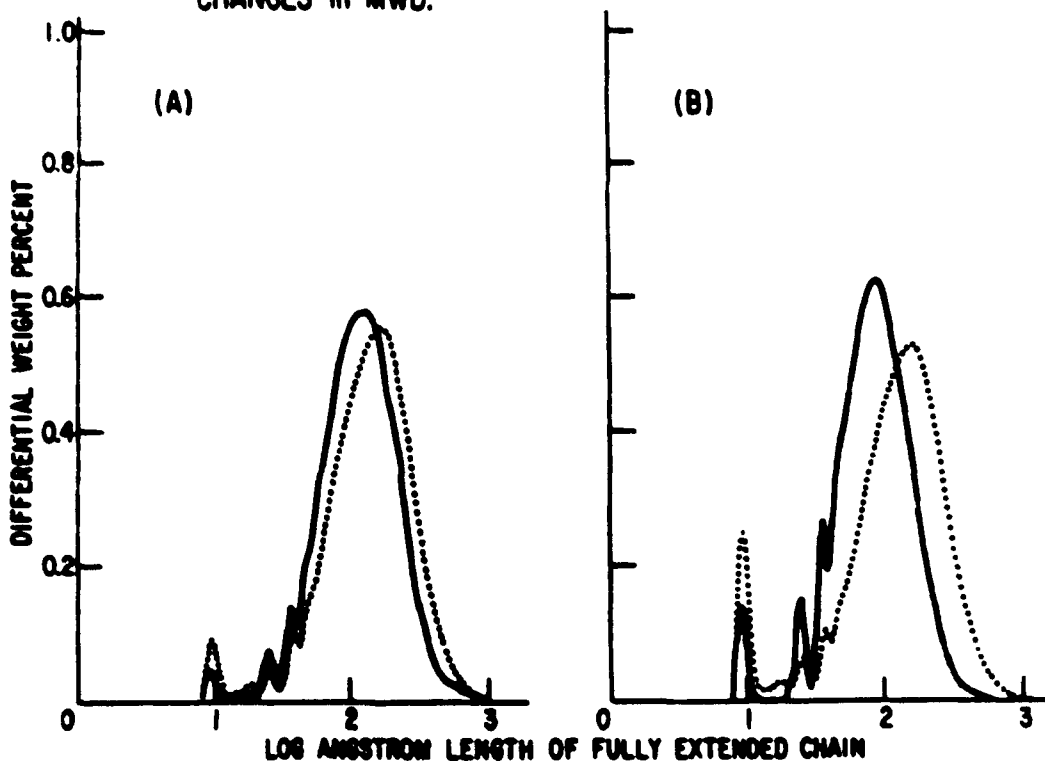
An Estol B, M. W. 2031 blended with 0.60 mole 1,4-BDO and containing 3.5 ppm of TEHT catalyst decreased in $\bar{M}_w$ from 124.4Å to 115.9Å (7%) after 4 weeks at 93°C. But the same blend containing 22 ppm of TEHT

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Figure 1. EFFECT of 1,4-BDO CONCENTRATION on the ALCOHOLYSIS of ESTOL B/1,4-BDO BLENDS on 4 WEEKS/93°C AGING. CHANGES in MWD.



(A) 0.80 mole 1,4-BDO per 1.00 mole ESTOL B (M.W. 2031), 22 ppm^{*} TENT CATALYST (Exp. 7746-74-18-1).

(B) 2.00 moles 1,4-BDO per 1.00 mole ESTOL B (M.W. 2031), 19 ppm^{*} TENT CATALYST (Exp. 7746-74-18-5).

----- ORIGINAL MWD
 ——— MWD after 4 WEEKS at 93°C

* Based on blend (in above and always).

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catalyst decreased in M_w from 128.7 Å to 111.2 Å (14%) after the same exposure.

Normalized GPC graphs for both blends before and after aging are shown in Figure 2 (A&B). The data show that the major peak in (B) (blend contains 22 ppm TEHT) has shifted more to the lower molecular weight range than (A) (blend contains only 3.5 ppm TEHT catalyst).

2. Effective Stabilizers

Since it has been found that the presence of TEHT catalyzes the alcoholysis of the polyester by the free 1,4-BDO in the blend, our approach in finding a stabilizer was to seek one that would chelate the titanium in the blend and thus render it inactive. We have examined a number of potential chelators for this purpose and have found that some of them are effective blend stabilizers. Their effectiveness will now be described and discussed.

A. Quinollinol Effect on Blend MWD (by GPC) and 1,4-BDO Content (by GPC)

Quinollinol (8-hydroxy quinolline) was found to be the most effective of all of the stabilizers investigated in this study. Aging data for blends made from Estol B (M.W. 2032) with 0.60 moles of 1,4-BDO are shown in Table I.

TABLE I

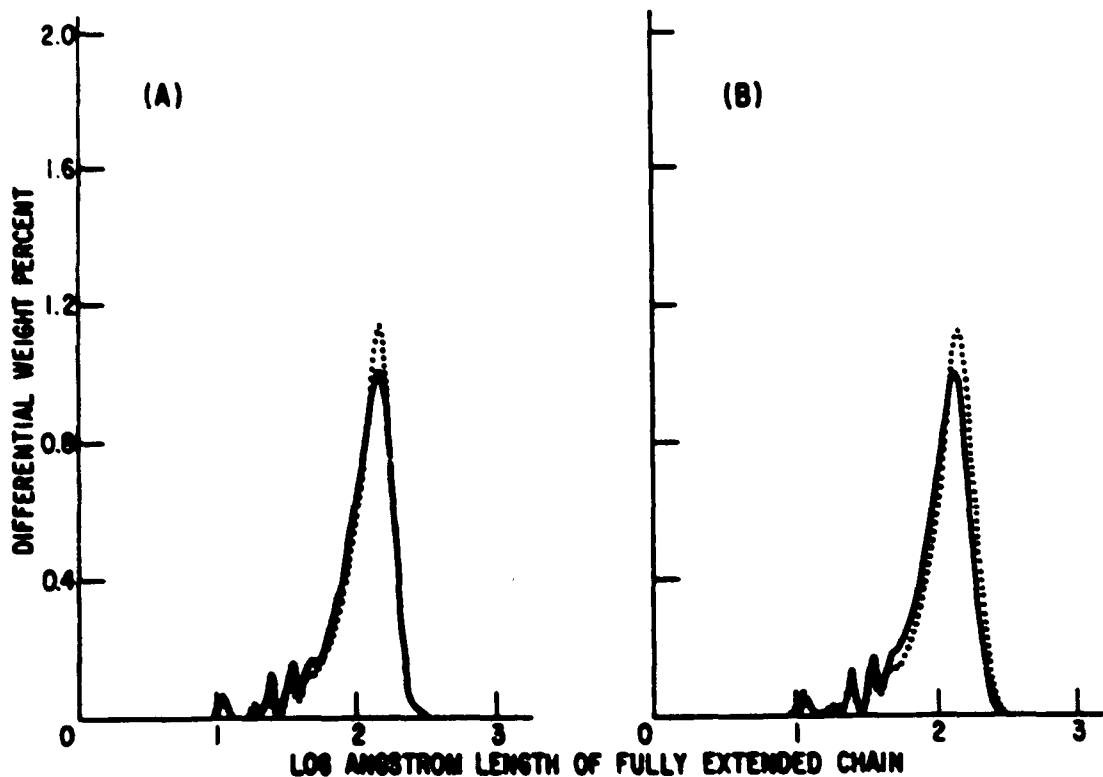
Changes in MWD Determined by GPC in Estol B (M.W. 2032)
/0.60 mole 1,4-BDO Blend Containing Quinollinol Stabilizer
on Heat Aging at 93°C.

7745-74	5-1	5-3	5-4	5-6	18-1	18-2	19-3
TEHT (ppm)	3.5	3.5	22	22	22	22	22
Quinollinol (%)	0	0.04	0	0.04	0	0.4	0.8
Original	124	128	129	130	170	164	168
After 24 hrs.	-	124 (97)	125 (97)	126 (97)			
72 hrs.	118 (95)	129 (100)	127 (98)	127 (97)			
1 wk.	118 (95)	128 (100)	126 (97)	131 (100)			
2 wks.	117 (94)	125 (97)	117 (91)	117 (90)			
4 wks.	116 (94)	128 (100)	111 (86)	121 (93)	144 (85)	166 (100)	168 (100)

Numbers in parentheses indicate percent retention of original value ($\bar{M}_w$).

Table I data show that quinollinol at the 0.04% level offers complete stability to the blend containing 3.5 ppm of TEHT for 4 weeks at 93°C. The control blend after the same exposure retains 94% of its original M_w .

Figure 2. EFFECT of TEHT CATALYST LEVEL on the ALCOHOLYSIS of ESTOL B (M.W. 2031)/0.60 mole 1,4-BDO BLEND on 4 WEEK/93°C AGING. CHANGES in MWD.



- (A) 3.5 ppm *tetrakis*(2-ETHYL HEXYL) TITANATE CATALYST (Exp. 7745-74-5-1)
 (B) 22 ppm *tetrakis*(2-ETHYL HEXYL) TITANATE CATALYST (Exp. 7745-74-5-4)

..... ORIGINAL MWD
 ——— MWD after 4 WEEKS at 93°C

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When the TEHT level was increased to 22 ppm the same low level of quinolinol (0.04%) did not give total protection but allowed 93% retention of the original $\bar{M}_w$ after 4 wks. at 93°C. The control in this case retained 86% of the original $\bar{M}_w$.

To obtain a completely stable blend containing 22 ppm of TEHT the quinolinol level was increased to 0.4 and 0.8%. In both cases total blend stability was obtained after 4 wks. at 93°C. The unstabilized control blend lost 15% of its original $\bar{M}_w$ after the same exposure.

The difference in original molecular weights in both sets of experiments is due to the different columns used in the GPC determinations. Blend series No. 5 was obtained with 5 columns of maximum pore size - 60Å, 100Å, 100Å, 500Å, and 1000Å, 567 plates/foot. Blend series No. 18 was obtained with five columns of maximum pore size of 60Å, 100Å, 500Å, 700-1000Å, 10,000Å, 624.4 plates/foot.

The effect of quinolinol as stabilizer for Estol B (M.W. 2032)/1,4-BDO blends made with 2.00 moles of 1,4-BDO on heat aging at 93°C. is shown in Table II and in Figures 3 (A, B, C, D) and Figure 4 (A, B, C).

Table II gives changes on aging at 93°C. in blend weight average molecular weight ($\bar{M}_w$) determined by GPC and free 1,4-BDO content determined by gas chromatography (GC). Two sets of data are given, both sets are almost identical except for small differences in TEHT level which are not expected to affect the aging results. The different original $\bar{M}_w$ values for both sets of blends, which should be the same, are most likely caused by aging of the GPC columns (the pore size is reduced by shrinkage or contamination). Changes in the columns should not affect the relative $\bar{M}_w$ values within one set. The accuracy of the GC determinations is about $\pm 0.5\%$.

Table II data show that the % retention of $\bar{M}_w$ increases gradually with increasing quinolinol level from 78% retention of the original $\bar{M}_w$ at 0.10% quinolinol to total protection at 0.8% quinolinol after 4 weeks at 93°C. About 90% of the original $\bar{M}_w$ value is obtained at 0.20 to 0.30% quinolinol after the same exposure.

The GC data on the 1,4-BDO content of the blends agree reasonably well with the GPC data. Considering each set of data, we see that the retention of the original 1,4-BDO level increases with increasing quinolinol concentration in each set. Taking into account the experimental error of the method, we can conclude that about 90% of the original 1,4-BDO level is retained at quinolinol concentrations of 0.20 to 0.8% after 4 weeks aging at 93°C., while without a stabilizer the blend retains only about 50% of the original $\bar{M}_w$ and about 40% of the original 1,4-BDO content.

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TABLE II

Changes in MWD and 1,4-BDO Content of Estol B/1,4-BDO Blends
Made with 2.0 moles of 1,4-BDO and Stabilized with Quinolinol, on
93°C. Heat Aging

7745-75	69-1		69-5		69-6		69-7	
TEHT (ppm)	22		22		22		22	
Quinolol (%)	0		0.10		0.20		0.30	
	$\bar{M}_w, \lambda$	1,4-BDO	$\bar{M}_w, \lambda$	1,4-BDO	$\bar{M}_w, \lambda$	1,4-BDO	$\bar{M}_w, \lambda$	1,4-BDO
Original	230	9.0	229	10.1	217	9.8	213	8.9
After 1 wk.	140 (61)	7.1 (79)		9.6 (96)		9.7 (100)		9.2 (103)
3 wks.	107 (46)	4.4 (49)		8.5 (85)		9.0 (92)		9.0 (101)
4 wks.	95 (41)	2.8 (31)	179 (78)	8.4 (84)	185 (85)	8.6 (88)	197 (92)	8.8 (99)
7745-74	18-5		18-6		18-7			
TEHT (ppm)	19		19		19			
Quinolol (%)	0		0.4		0.8			
	$\bar{M}_w, \lambda$	1,4-BDO	$\bar{M}_w, \lambda$	1,4-BDO	$\bar{M}_w, \lambda$	1,4-BDO		
Original	158	8.7	157	9.1	157	8.5		
After 4 wks.	105 (66)	4.6 (53)	153 (97)	8.0 (88)	157 (100)	7.9 (93)		

All blends were made from Estol B (M. W. 2032).

Numbers in parentheses indicate percent retention of original values.

$\bar{M}_w$ was determined by gel permeation chromatography (GPC); percent 1,4-BDO content was determined by gas chromatography (GC).

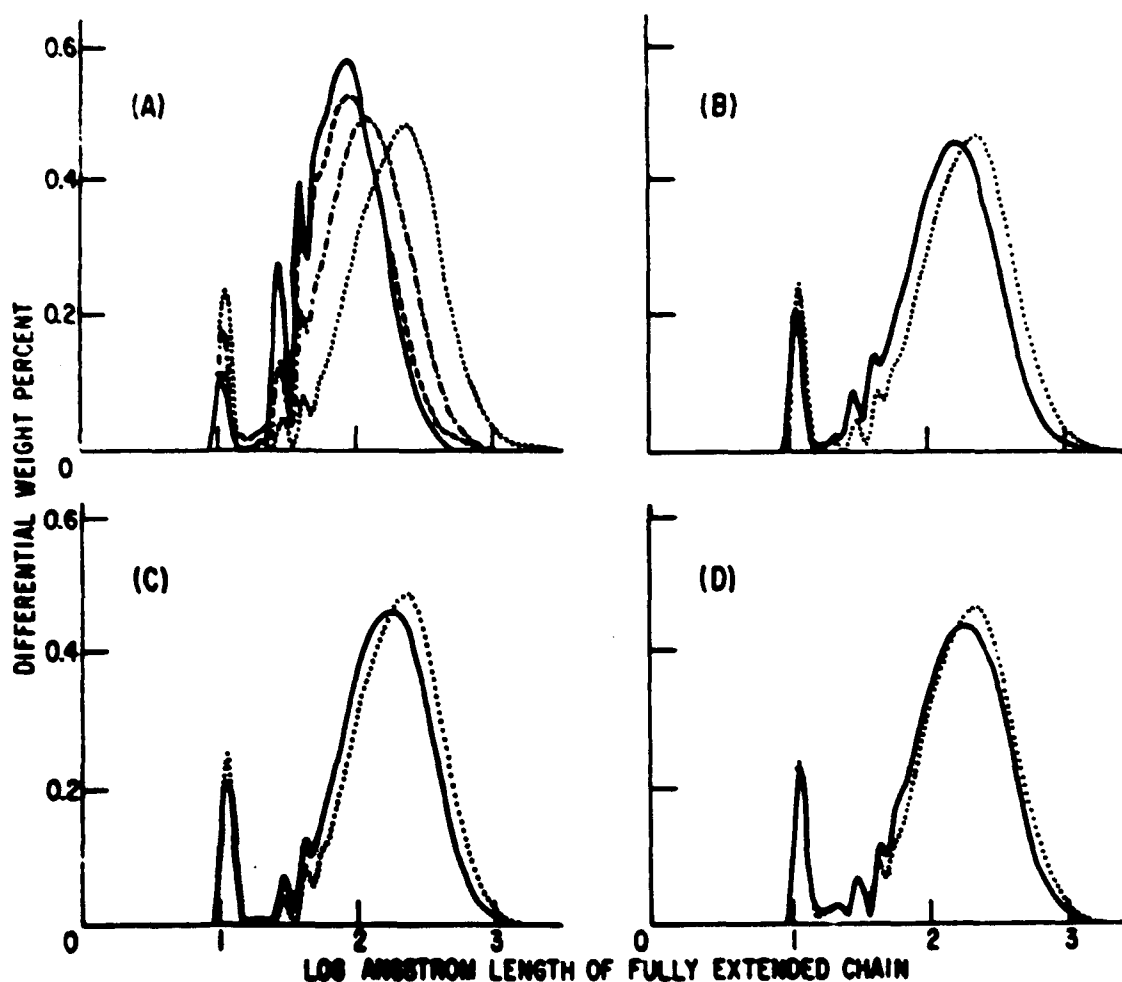
Complete normalized GPC curves of the blends discussed in Table II are shown in Figure 3 (A, B, C, D) and Figure 4 (A, B, C). The data for the unstabilized blend in Figure 3 shows that most of the changes take place during the first week of aging with fewer changes during the second and third weeks, and the least change during the fourth week of heat aging. Curves (B) and (C) containing 0.10% and 0.20% quinolinol show about the same changes after heat aging for 4 weeks at 93°C, but considerably less changes than the control blend (A). Curve (D) for the blend containing 0.30% quinolinol shows the fewest changes (practically no decrease in 1,4-BDO peak) after heat aging.

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Figure 3. EFFECT of QUINOLINOL LEVEL on the ALCOHOLYSIS of ESTOL B (M.W. 2023) / 2.00 mole 1,4-BDO BLEND CONTAINING 22 ppm TEHT on 93°C HEAT AGING. CHANGES in MWD.



(A) NO STABILIZER (Exp. 7745-74-69-1), (B) 0.10% QUINOLINOL (Exp. 7745-74-69-5),
(C) 0.20% QUINOLINOL (Exp. 7745-74-69-6), (D) 0.30% QUINOLINOL (Exp. 7745-74-69-7)

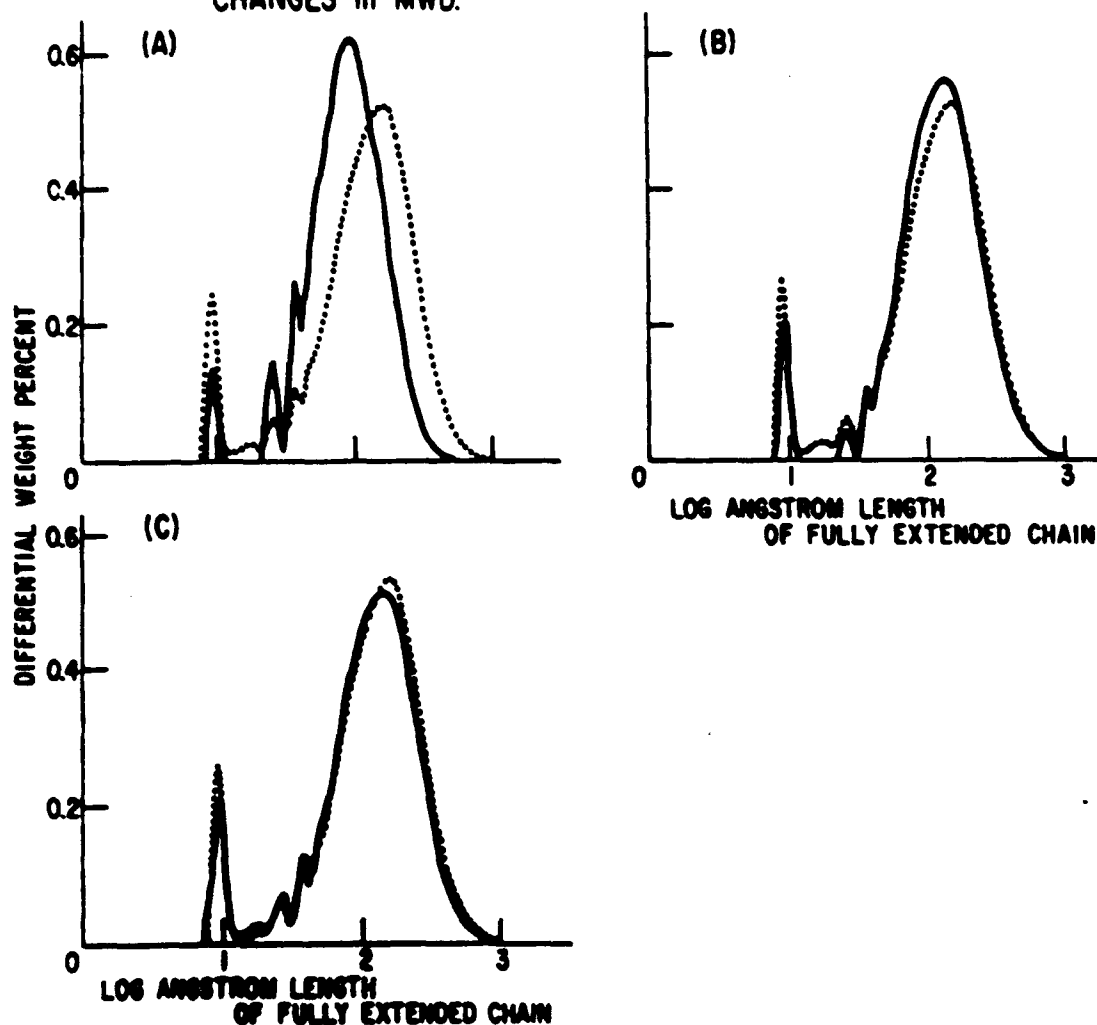
----- ORIGINAL MWD
----- MWD after 1 WEEK at 93°C
----- MWD after 3 WEEKS at 93°C
----- MWD after 4 WEEKS at 93°C

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Figure 4. EFFECT of QUINOLINOL LEVEL on the ALCOHOLYSIS of ESTOL B (M.W. 2032) / 2.00 mole 1,4-BDO BLEND CONTAINING 19 ppm of TEHT on 93°C HEAT AGING. CHANGES in MWD.



(A) NO STABILIZER (Exp. 7745-74-18-5), (B) 0.4% QUINOLINOL (Exp. 7745-74-18-6),
(C) 0.8% QUINOLINOL (Exp. 7745-74-18-7)

— ORIGINAL MWD
— MWD after 4 WEEKS at 93°C

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Figure 4 shows the blends containing 0.4 (B) and 0.8% (C) quinolinol along with an unstabilized control blend (A). Here we see that whereas the control blend has undergone considerable changes, both blends containing quinolinol have changed to a relatively small extent after heating for 4 weeks at 93°C. It should be recalled here that (C) (blend contains 0.8% quinolinol) did not show any changes in M_w after the same heating period (Table II).

**B. Acetyl Acetone Effect on Blend MWD (by GPC) and
1,4-BDO Content (by GC)**

I found that acetyl acetone (AcAc) is also an effective stabilizer against the alcoholysis of Estol B/1,4-BDO blends on heat aging, but that it is somewhat less effective than quinolinol. Supporting data are shown in Table III and in Figure 5 (A, B, C, D).

The GPC data indicate that about 70% of the original M_w value is retained after 4 weeks at 93°C. at the 0.2 and 0.3% AcAc level versus 41% retention for the unprotected control. In the case of quinolinol, about 90% of the original value was retained after the same exposure (Table II). The high value (86% retention) for blend 69-2 containing 0.10% AcAc is out of line and appears to be in error.

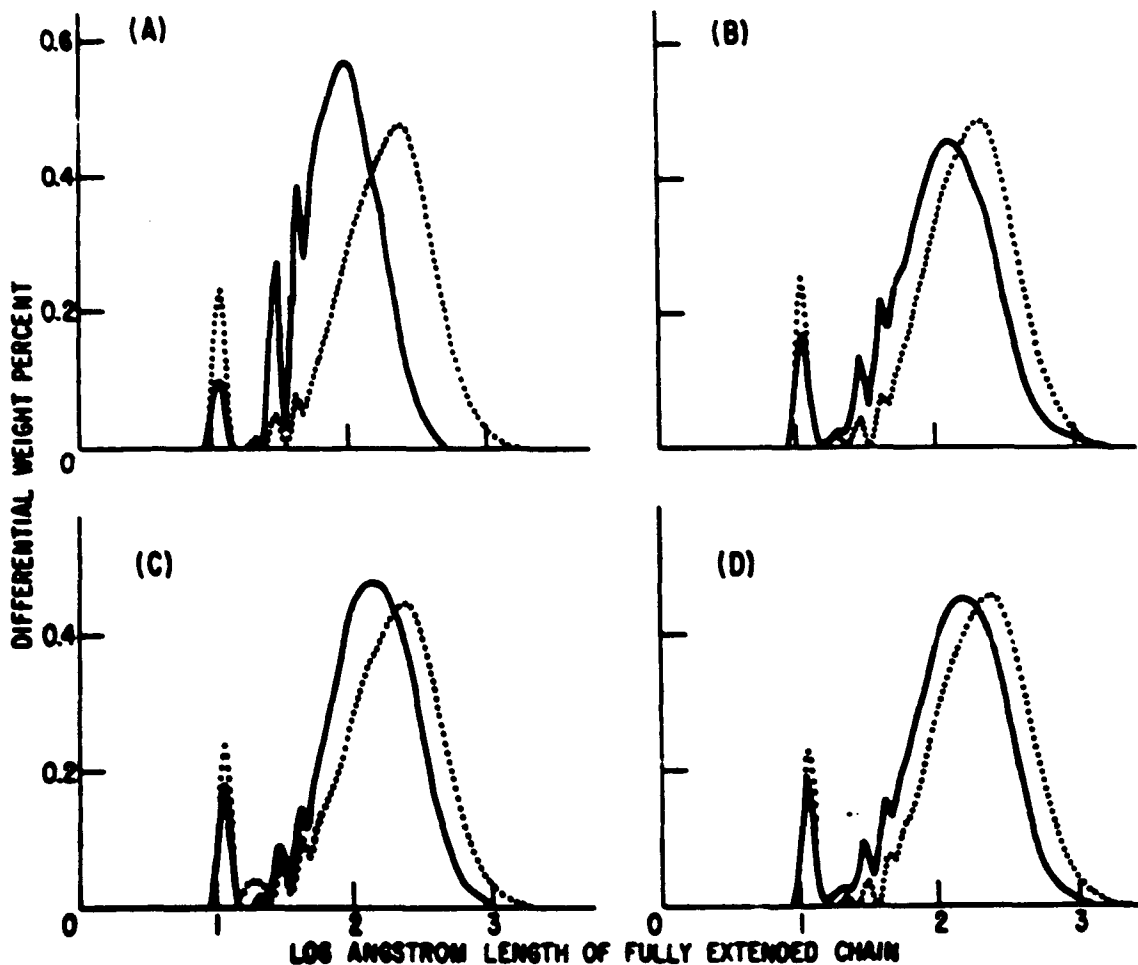
The normalized GPC curves in Figure 5 show that the AcAc-containing blends (B, C, D) undergo much fewer changes after 4 weeks aging at 93°C. than the unstabilized control (A) blend, but changes do occur.

Comparing Figure 5 with Figure 3, we see that the AcAc-containing blends undergo greater changes than the quinolinol-containing blends under the same heat aging conditions.

The changes in the 1,4-BDO content of the blends on heating, as determined by GC, are shown in Table III. The data on heat aging at 93°C. (series 6^a) show that about 80% of the original 1,4-BDO content is retained after 4 weeks of aging at all three AcAc levels. The data also show that very little loss in 1,4-BDO content takes place during the first three weeks of aging with a more rapid decrease in 1,4-BDO concentration during the fourth week. The control blend retains only 31% of the original 1,4-BDO content after the same exposure. The blends containing 0.20-0.30% of quinolinol (Table II) retained over 90% of the original 1,4-BDO amount after the same exposure.

Blend series 55 shows loss in 1,4-BDO content on aging at 100°C. We see that at the higher temperature the blend containing 0.10% AcAc loses free 1,4-BDO slightly faster during the entire aging period than the corresponding blend at 93°C. No significant differences in 1,4-BDO loss between the two aging temperatures can be seen for the unstabilized control blends.

Figure 5. EFFECT of ACETYL ACETONE LEVEL on the ALCOHOLYSIS of ESTOL B (M.W. 2032) / 2.00 mole 1,4-BDO BLEND CONTAINING 22 ppm TEHT on 93°C HEAT AGING. CHANGES in MWD.



(A) NO STABILIZER (Exp. 7745-74-69-1), (B) 0.10 % ac ac (Exp. 7745-74-69-2),
 (C) 0.20 % ac ac (Exp. 7745-74-69-3), (D) 0.30 % ac ac (7745-74-69-4).

..... ORIGINAL MWD
 — MWD after 4 WEEKS at 93°C

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TABLE III

Changes in MWD and 1,4-BDO Content of Estol B/1,4-BDO Blends
Made with 2.0 moles of 1,4-BDO and Stabilized with Acetyl Acetone
on 93°C. Heat Aging

7745-75 AcAc (%)	69-1 0		69-2 0.10		69-3 0.20		69-4 0.30	
	$\overline{M}_w, \text{\AA}$	1,4-BDO	$\overline{M}_w, \text{\AA}$	1,4-BDO	$\overline{M}_w, \text{\AA}$	1,4-BDO	$\overline{M}_w, \text{\AA}$	1,4-BDO
Original	230	9.0	215	9.1	234	9.0	244	10.3
After 1 wk.	140 (61)	7.1 (79)		10.1 (111)		9.6 (107)		9.9 (96)
@ 93°C 3 wks.	107 (46)	4.4 (49)		8.9 (98)		9.5 (105)		8.6 (83)
4 wks.	95 (41)	2.8 (31)	185 (86)	6.9 (76)	165 (70)	7.8 (87)	171 (70)	8.3 (81)
7745-75 AcAc (%)	55-1 0		55-3 0.10					
	<u>1,4-BDO</u>		<u>1,4-BDO</u>					
Original	9.5		10.5					
After 2 wks.	4.6 (48)		8.7 (83)					
@ 100°C.								
" 3 wks.	-		8.2 (78)					
" 4 wks.	3.3 (35)		7.0 (67)					

All blends were made from Estol B, M.W. 2032, containing 22 ppm TEHT catalyst.

Numbers in parentheses indicate percent retention of original values.

$\overline{M}_w$ was determined by GPC; percent 1,4-BDO content was determined by gas chromatography.

C. N,N,N',N'-Tetra-n-butyl Ethylenediaminetetraacetate (TBEDTA)
Effect on 1,4-BDO Content (By GC)

EDTA or its sodium salts are known to be good chelators for titanium, but in our experience EDTA was ineffective as an Estol B/1,4 BDO blend stabilizer. I feel that the ineffectiveness of EDTA as a blend stabilizer is due to its insolubility in the blend. Furthermore, even if effective, EDTA being a free acid would likely decrease the hydrolytic resistance of Estane made from EDTA-containing blends. To overcome these difficulties, I prepared TBEDTA which is readily soluble in the blends and has relatively low acidity (acid number: found, 0.8; theoretical AN of EDTA is 768).

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TBEDTA was evaluated as stabilizer in a blend made from Estol B, M. W. 2032, and 2.0 moles 1,4-BDO and containing 21 ppm TEHT catalyst. The data obtained by GC and showing the loss of free 1,4-BDO on heat aging are presented in Table IV. The data show that a blend containing 0.20% TBEDTA retains 83% of its original 1,4-BDO content. This value is very close to the value (87%) obtained with 0.20% AcAc after the same exposure (Table III, #69-3). But since the control polymer in the TBEDTA series lost much less 1,4-BDO on exposure (50%) vs. the control polymer in the AcAc series (31%) an exact comparison between these two stabilizers is not possible. Nevertheless, the data show that TBEDTA is an effective stabilizer but it appears to be less effective than AcAc.

TABLE IV

Changes in the 1,4-BDO Content of Estol B (M. W. 2032)/
2.00 mole 1,4-BDO Blends Containing 21 ppm TEHT Catalyst
and Stabilized with TBEDTA on 93°C. Heat Aging

7745-75-161	1	2	3	4	5
TBEDTA (%)	0	0.05	0.10	0.20	0.30
	<u>% 1,4-BDO In Blend</u>				
Original	8.2	8.0	8.1	8.2	8.3
After 3 weeks	4.6 (56)	6.2 (77)	6.5 (80)	6.8 (83)	6.9 (83)
" 4 weeks	4.1 (50)	6.0 (75)	6.3 (78)	6.8 (83)	6.8 (83)

Numbers in parentheses indicate percent retention of original values

3. Other Compounds that have been Evaluated as Estol B- 1,4-BDO Blend Alcoholysis Stabilizers

Of the other compounds that have been evaluated as Estol B-1,4-BDO blend alcoholysis stabilizers, tannic acid showed the most effectiveness. For example, a blend made from Estol B (M. W. 2032) and 0.60 mole of 1,4-BDO, and containing 22 ppm TEHT and 0.8% tannic acid retained 93% of its original M_w after 4 weeks at 93°C. Under the same conditions, the unstabilized control blend retained only 85%, but the quinolinol-containing blend retained 100%. The effective concentration of tannic acid in the blend was less than 0.8% since most of the additive did not dissolve.

Ethylene diamine tetraacetic acid (EDTA) showed no effect as a stabilizer, but this may be due to the insolubility of the EDTA in the blend.

Other compounds that were evaluated as stabilizers and were soluble in the blend, but showed no effectiveness, were 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione; 2,2'-bipyridine, 1,2-dimethoxy ethane and Inhibitor NPH.

4. Effect of Quinolinol and Acetyl Acetone on Estol B-1,4-BDO Blend Color Stability During Ambient Storage

Discoloration of Estol B/1,4-BDO blends containing from 0.30 to 0.80% of quinolinol was observed on storage of samples exposed to light. The blends were stored in closed screwcap glass bottles on the bench top. After 3 months of storage, it was observed that the top and sides of the solid blend had turned brown, whereas the bottom had changed little in color. This discoloration was observed in blends containing 22 ppm of TEHT catalyst and also in blends made from unwashed stannous chloride catalyzed Estol B. The discoloration is definitely a surface effect since the interior of the sample is not affected.

There appears to be no significant color problem in the blends containing acetyl acetone. After 4 months storage on the bench top a blend made from stannous chloride catalyzed Estol B and containing 0.30% AcAc showed only slight yellowing.

5. Effect of Quinolinol and Acetyl Acetone on Estane 5701

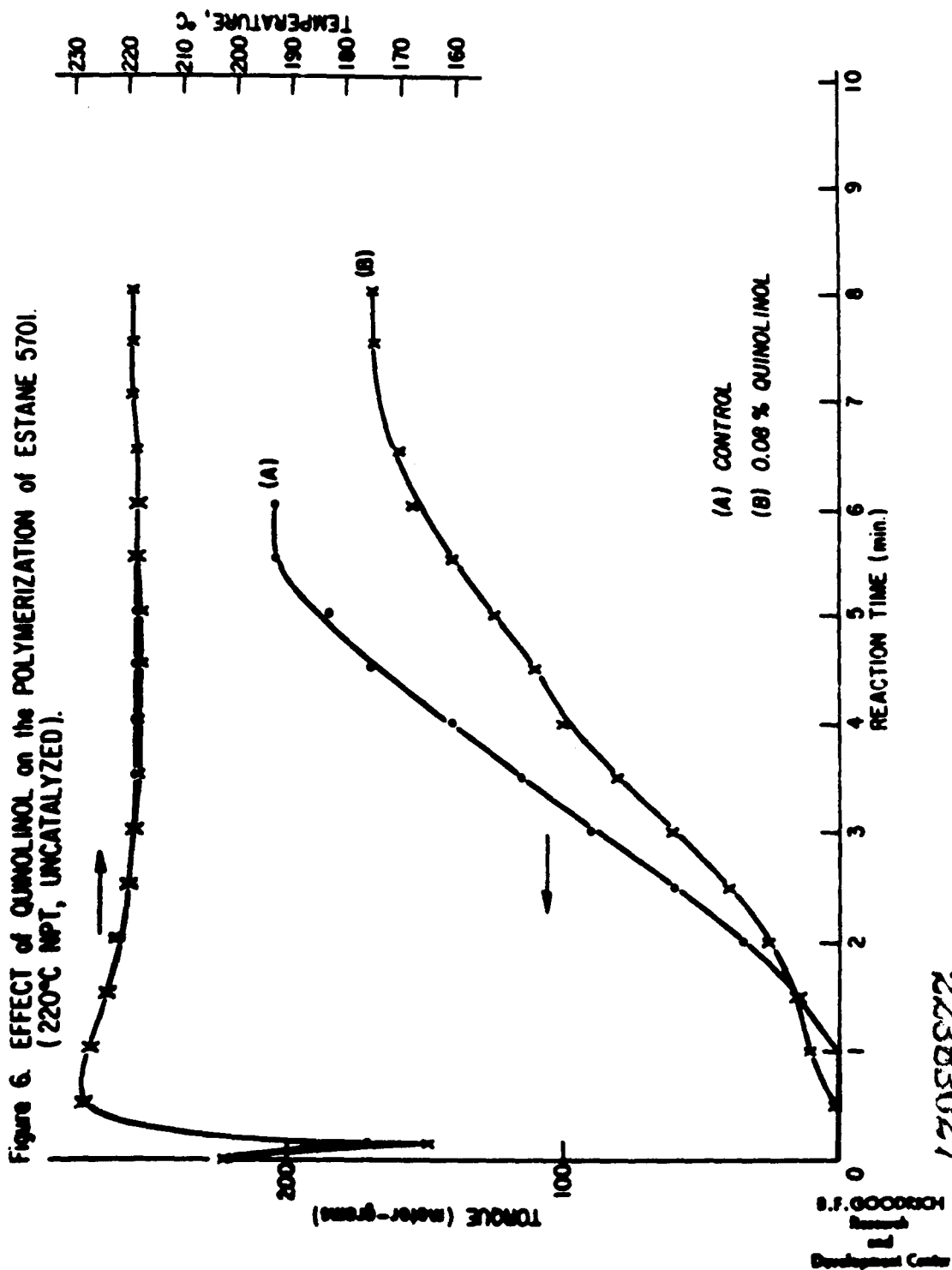
A. Polymerisation

The effect of 0.08% quinolinol on the 220°C. NPT[®], uncatalyzed, random melt polymerization of Estane 5701 in the Brabender Plasticorder Reactor (BPR) is shown in Figure 6. Stannous chloride catalyzed, water washed Estol B (Sec. 1 IG) was used in these experiments. Figure 6 data show that the quinolinol-containing reaction mixture (7741-74-223)(B) polymerized somewhat slower, and did not reach as high a final polymerizate torque as the control polymer (7741-74-223)(A). But the difference was not great, as would be expected since the system contained no effective residual metal catalyst to be deactivated by the chelator.

At maximum torque (8 min. reaction time) the quinolinol-containing polymer had a DSV of 0.64 when quenched in methanol immediately; without methanol quenching it grew to a DSV value of 1.57 in 10 days. The corresponding DSV values for the control polymer were 0.67 (methanol quenched after 6 minutes pzn.) and 1.71 (unquenched, aged 10 days).

The effect of a higher level of quinolinol (0.5%) on the polymerization of Estane 5701 was evaluated in the BPR at 170°C NPT[®] using Production Estol B'

[®]Nominal polymerization temperature



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1,4-BDO blend (Sec. I 3) containing 10 ppm TEHT catalyst (6.7 ppm TEHT by X-ray fluorescence) and Production MDI (Sec. I 3A). The data (Figure 7) show that the quinolinol has reduced the rate of polymerization considerably and that at 12 min. reaction time the torque of the polymerizate for the quinolinol-containing polymer (B) (7742-76-321) is less than for the control polymer (A) (7745-76-175).

At 12 min. reaction time the quinolinol-containing polymer had a DSV of 0.88 when quenched in methanol immediately; without methanol quenching it grew to a DSV value of 1.57 in 4 weeks. The corresponding DSV values for the control polymer were 0.99 (methanol quenched after 12 min. pzn.) and 1.53 (unquenched, aged 4 weeks).

In this case the retarding effect of quinolinol was obviously due to the chelation of the residual TEHT catalyst from Estol B manufacture by the quinolinol. As the unquenched DSV data show, the quinolinol has only a retarding effect on the polymerization rate but does not limit the final polymer growth on shelf aging.

The effect of 0.3% quinolinol on the polymerization of Estane 5701 was evaluated in a polymerization run in a beaker. Production Estol B (Sec. I 1F) containing 10 ppm of TEHT catalyst was used in these experiments. It was observed that the quinolinol had a noticeable retarding effect on the polymerization. The control polymer (7742-75-194) could be stirred for only 1-1/4 min. due to a rapid increase in viscosity, whereas the polymer containing the quinolinol (7745-75-81) was still fluid at 2 min. reaction time.

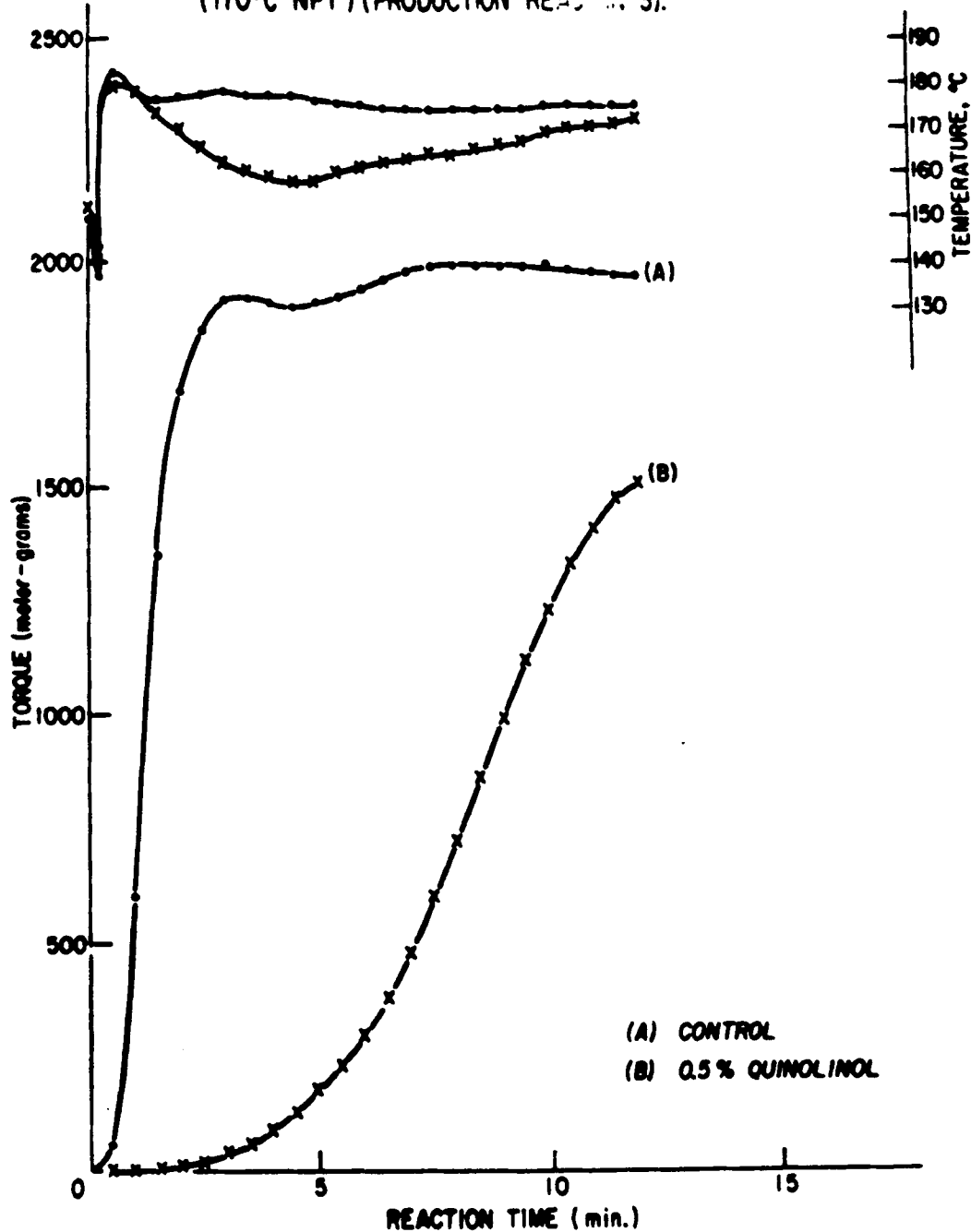
The effect of acetyl acetone on the polymerization reaction was evaluated in a beaker polymerization (7745-75-79) using the same reactants as in the case of quinolinol above. AcAc was also observed to have a retarding effect on the polymerization, but less so than quinolinol. The polymerizing mixture could easily be stirred for 1-3/4 min., and at this point the viscosity of the melt was not extremely high.

B. Original Properties and Environmental Resistance

The effect of two levels of quinolinol (0.10 and 0.30%) on the properties and aging characteristics of Estane 5701 is shown in Table V. For each concentration of quinolinol a different set of reactants was used.

A level of 0.10% quinolinol was evaluated in a polymer made from stannous chloride catalyzed, water washed Estol B (Sec. I 1E), Mobay MDI (Sec. I 3A), and distilled 1,4-BDO (Sec. I 2C). In addition 0.30% quinolinol was evaluated in polymer made from Production Estol B (Sec. I 1F) which had been catalyzed with 10 ppm TEHT, Upjohn MDI (Sec. I 3B) and Production 1,4-BDO (Sec. I 2D).

Figure 7. EFFECT of QUINOLINOL on the POLYMERIZATION of ESTANE 5701.
(170°C NPT) (PRODUCTION REACTANTS).



(A) CONTROL
(B) 0.5% QUINOLINOL

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TABLE V
Effect of Quinoline on the Original Properties and Environmental Resistance of Estane 5701

7745-74 7745-75 7745-76 Extruded B.M.W., Cal.	21		22		23		24		25		26		27	
	1104, SeCl ₄ , washed		1104, SeCl ₄ , washed		1104, SeCl ₄ , washed		1104, SeCl ₄ , washed		1104, SeCl ₄ , washed		1104, SeCl ₄ , washed		1104, SeCl ₄ , washed	
	Quinoline (7% mil)	Temp. Str. (psi)	Quinoline (7% mil)	Temp. Str. (psi)	Quinoline (7% mil)	Temp. Str. (psi)	Quinoline (7% mil)	Temp. Str. (psi)	Quinoline (7% mil)	Temp. Str. (psi)	Quinoline (7% mil)	Temp. Str. (psi)	Quinoline (7% mil)	Temp. Str. (psi)
T _g , °C	157	157	157	157	157	157	157	157	157	157	157	157	157	157
Original (7% mil)	8500	8500	8500	8500	8500	8500	8500	8500	8500	8500	8500	8500	8500	8500
After 3 days at 140°C (b)	6200 (73)	6200 (73)	6200 (73)	6200 (73)	6200 (73)	6200 (73)	6200 (73)	6200 (73)	6200 (73)	6200 (73)	6200 (73)	6200 (73)	6200 (73)	6200 (73)
After 7 days at 140°C (b)	7400 (87)	7400 (87)	7400 (87)	7400 (87)	7400 (87)	7400 (87)	7400 (87)	7400 (87)	7400 (87)	7400 (87)	7400 (87)	7400 (87)	7400 (87)	7400 (87)
Original (2% mil)	9100	9100	9100	9100	9100	9100	9100	9100	9100	9100	9100	9100	9100	9100
After 44 hrs. CAWO	2600 (29)	2600 (29)	2600 (29)	2600 (29)	2600 (29)	2600 (29)	2600 (29)	2600 (29)	2600 (29)	2600 (29)	2600 (29)	2600 (29)	2600 (29)	2600 (29)
After 80 hrs. CAWO	1700 (19)	1700 (19)	1700 (19)	1700 (19)	1700 (19)	1700 (19)	1700 (19)	1700 (19)	1700 (19)	1700 (19)	1700 (19)	1700 (19)	1700 (19)	1700 (19)
After 154 hrs. CAWO	1100 (12)	1100 (12)	1100 (12)	1100 (12)	1100 (12)	1100 (12)	1100 (12)	1100 (12)	1100 (12)	1100 (12)	1100 (12)	1100 (12)	1100 (12)	1100 (12)
Original (2% mil)	8600	8600	8600	8600	8600	8600	8600	8600	8600	8600	8600	8600	8600	8600
After 1 wk. in 70°C water	2500 (29)	2500 (29)	2500 (29)	2500 (29)	2500 (29)	2500 (29)	2500 (29)	2500 (29)	2500 (29)	2500 (29)	2500 (29)	2500 (29)	2500 (29)	2500 (29)
After 2 wks. in 70°C water	2100 (24)	2100 (24)	2100 (24)	2100 (24)	2100 (24)	2100 (24)	2100 (24)	2100 (24)	2100 (24)	2100 (24)	2100 (24)	2100 (24)	2100 (24)	2100 (24)
After 3 wks. in 70°C water	1800 (21)	1800 (21)	1800 (21)	1800 (21)	1800 (21)	1800 (21)	1800 (21)	1800 (21)	1800 (21)	1800 (21)	1800 (21)	1800 (21)	1800 (21)	1800 (21)
After 4 wks. in 70°C water	1600 (18)	1600 (18)	1600 (18)	1600 (18)	1600 (18)	1600 (18)	1600 (18)	1600 (18)	1600 (18)	1600 (18)	1600 (18)	1600 (18)	1600 (18)	1600 (18)
After 5 wks. in 70°C water	1400 (16)	1400 (16)	1400 (16)	1400 (16)	1400 (16)	1400 (16)	1400 (16)	1400 (16)	1400 (16)	1400 (16)	1400 (16)	1400 (16)	1400 (16)	1400 (16)
After 9 wks. in 70°C water	450 (5)	450 (5)	450 (5)	450 (5)	450 (5)	450 (5)	450 (5)	450 (5)	450 (5)	450 (5)	450 (5)	450 (5)	450 (5)	450 (5)

(a) 0.4g/dl DMF + 0.05% n-Pr stabilizer.
(b) Values in parenthesis indicate percent retention of original value.

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Table V data show that there are some (expected) differences between the two control polymers. The polymer made from Production Estol B (contains active residual TEHT catalyst) and Production reactants has a higher DSV and a higher T_g value than the polymer made from laboratory Estol B (catalyzed with stannous chloride, then washed (deactivated) with water) Mobay MDI, and distilled 1,4-BDO. The Production reactant polymer also contains gel.

Aging data indicate that the Production reactant shows poorer oven aging and hydrolysis resistance than the laboratory reactant polymer. We suspect that the residual, active TEHT catalyst is the major cause for the poorer aging characteristics of polymers made from the Production reactant system.

The data show that quinolinol at the 0.10% level has no effect on the environmental resistance of Estane 5701 except to produce a very slight darkening in oven aged samples.

Considering the polymer with 0.30% quinolinol, we can see that the quinolinol has reduced the original DSV of the polymer by about 1/3, but has reduced the amount of gel to a great extent. But since the DSV of the quinolinol-containing polymer is very high, the addition of quinolinol produced no significant changes in the original stress-strain or T_g values of the polymer.

Considering the aged properties we see that the quinolinol appears to somewhat improve the oven aging resistance of the polymer. No quinolinol effect on other aging tests was noted except a very slight darkening of the samples after oven or water aging.

The polymer containing 0.5% quinolinol (7742-76-321, Fig. 7B) was molded to a 25 mil sheet and exposed in the carbon arc Weatherometer together with a control polymer (7745-76-175, Fig. 7A) to observe color formation. The data obtained are shown in Table VI.

Table VI data show that although the original color of the quinolinol-containing polymer (B) was better than that for the control on CAWO exposure, the quinolinol-containing polymer discolored more than the control polymer. It should be pointed out here that 0.5% quinolinol on the polymer is an excessive stabilizer level since adequate stabilization can be obtained with 0.3% quinolinol on the blend, which amounts to 0.2% quinolinol on the polymer in the case of Estane 5701. I expect to see less discoloration with lower levels of quinolinol in the polymer.

An adverse aspect of quinolinol is the strong medicinal odor that it imparts to the polymer. This odor becomes stronger at elevated temperatures, as during processing.

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TABLE VI

The Effect of 0.5% Quinololinol on the Color Formation of
Estane 5701 on Carbon Arc Weatherometer Exposure

Polymer Quinololinol (%) Hours in CAWO	Reflectance (Blue Filter, Base 73)	
	A 0	B 0.5
0	57	59
3	56	49
5	55	46
8	51	41
11	48	38
16	43	34
22	40	31
44	32	26
88	26	23
154	23	21

The effect of 0.30% of acetyl acetone on the original properties and environmental resistance of Estane 5701 can be seen in Table VII. The same Production raw materials (including TEHT-catalyzed Estol B) were used in this study as were used in the above evaluation of 0.30% quinololinol.

Original property data show that the addition of acetyl acetone has reduced the DSV and gel content of the polymer by a significant amount, but the DSV value is again still very high. A reduction in the T_g value is also noticeable, but the T_g reduction caused by the addition of the stabilizer has no effect on the original stress-strain properties of the polymer.

Table VII data on the aged polymers show that the AcAc has practically no effect on the aging characteristics of the polymer except a reduction in elongation after 154 hours in the carbon arc Weatherometer and possibly a slightly greater loss in tensile strength after 2 and 3 weeks exposure in water at 70°C.

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TABLE VII

Effect of Acetyl Acetone on the Original Properties and
Environmental Resistance of Estane 5701

7742-75	194 & 195					
7745-75			79			
Acetyl Acetone (%)	0		0.30			
DSV ^a	3.42, 43% gel.		2.18, 3% gel.			
T ₁ /T ₂ , °C.	-4/171		1/163			
	<u>Tens.Str.</u> (psi)	<u>300% M.</u> (psi)	<u>Elong.</u> (%)	<u>Tens.Str.</u> (psi)	<u>300% M.</u> (psi)	<u>Elong.</u> (%)
Originals (75 mil)	8500	1400	480	8900	1300	505
After 3 days @ 140°C. ^b	5200(61)	1000(71)	520(108)	5200(58)	990(76)	525(104)
" 7 days "	4500(53)	500(39)	560(116)	4700(53)	600(46)	565(112)
Originals (25 mil)	9700	1600	470	10200	1600	495
After 44 hrs. CAWO	2800(29)	1700(106)	355(75)	2400(23)	1700(106)	360(73)
" 88 "	1500(15)	1500(94)	290(62)	1400(14)	-	270(54)
" 154 "	1200(12)	-	200(42)	1200(12)	-	75 (15)
Originals (25 mil)	10400	1600	475	10200	1500	490
After 1 wk. in 70°C water	9800(94)	1900(119)	500(105)	10100(99)	1900(127)	520(106)
" 2 wks. "	8900(86)	1900(119)	520(110)	7900(77)	1700(113)	535(109)
" 3 wks. "	7500(72)	1600(100)	590(124)	6400(63)	1600(102)	585(119)
" 6 wks. "	1000(10)	900(56)	365(77)	1000(10)	900(60)	460(94)
" 9 wks. "	400(4)	-	20(4)	300(3)	-	30(6)

(a) 0.4g/dl DMF + 0.05% n-PrI.

(b) Numbers in parenthesis indicate percent retention of original value.

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II Stannous Chloride-Containing Estol B/1,4-BDO Blend Alcoholysis Stability

Another approach to the Estol B/1,4-BDO blend alcoholysis stability problem is to substitute TEHT polyesterification catalyst, which promotes the alcoholysis reaction, with some other polyesterification catalyst which does not promote this reaction, or that easily (preferably spontaneously) deactivates after/during polyesterification.

Stannous chloride dihydrate ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$) has been routinely used as polyesterification catalyst to produce low acid number polyester glycols at Brecksville since about 1964, following a patented method (5) adapted to Estol B by F. D. Stewart (6, 7). We have now found that stannous chloride polyesterification catalyst is practically inactive as an alcoholysis catalyst for Estol B/1,4-BDO blends on heat aging.

1. Heat Stability of Estol B/1,4 BDO Blends Made with Washed Estol B

Stannous chloride hydrolyzes readily to a water-insoluble basic chloride, $\text{Sn(OH)Cl} \cdot \text{H}_2\text{O}$ (7) which has no apparent catalytic activity with respect to urethane formation and apparently none in the polyesterification reaction. The same basic chloride forms during atmospheric oxidation with the simultaneous formation of stannic chloride according to Equation II (7).



Since the Estol B prepared in this laboratory is routinely water washed we assume that any residual stannous chloride has been converted to the basic chloride.

A. Changes in Estol B/1,4-BDO Blend MWD (by GPC)

Figure 8 (A) shows that a blend (7745-74-18-8) made from stannous chloride - catalyzed, water washed Estol B (Sec. I 1B) with 2.0 moles 1,4-BDO is practically completely stable on heat aging. The normalized GPC curves of the original blend and of the blend after 4 weeks aging at 93°C. are essentially superimposable. The $\bar{M}_w$ value of the original blend was 147Å. After heat aging it was 149Å.

The changes in the same blend heated for 4 weeks at 100°C. are shown in Figure 8 (B) (Blend 7745-74-58-1). The normalized GPC curves here are also practically superimposable, but a slight shift to lower molecular weight after heat aging is apparent in the blend aged at 100°C. (B). The $\bar{M}_w$ value for the original blend is 158Å, after heat aging it was reduced to 147Å (93% retention of the original value).

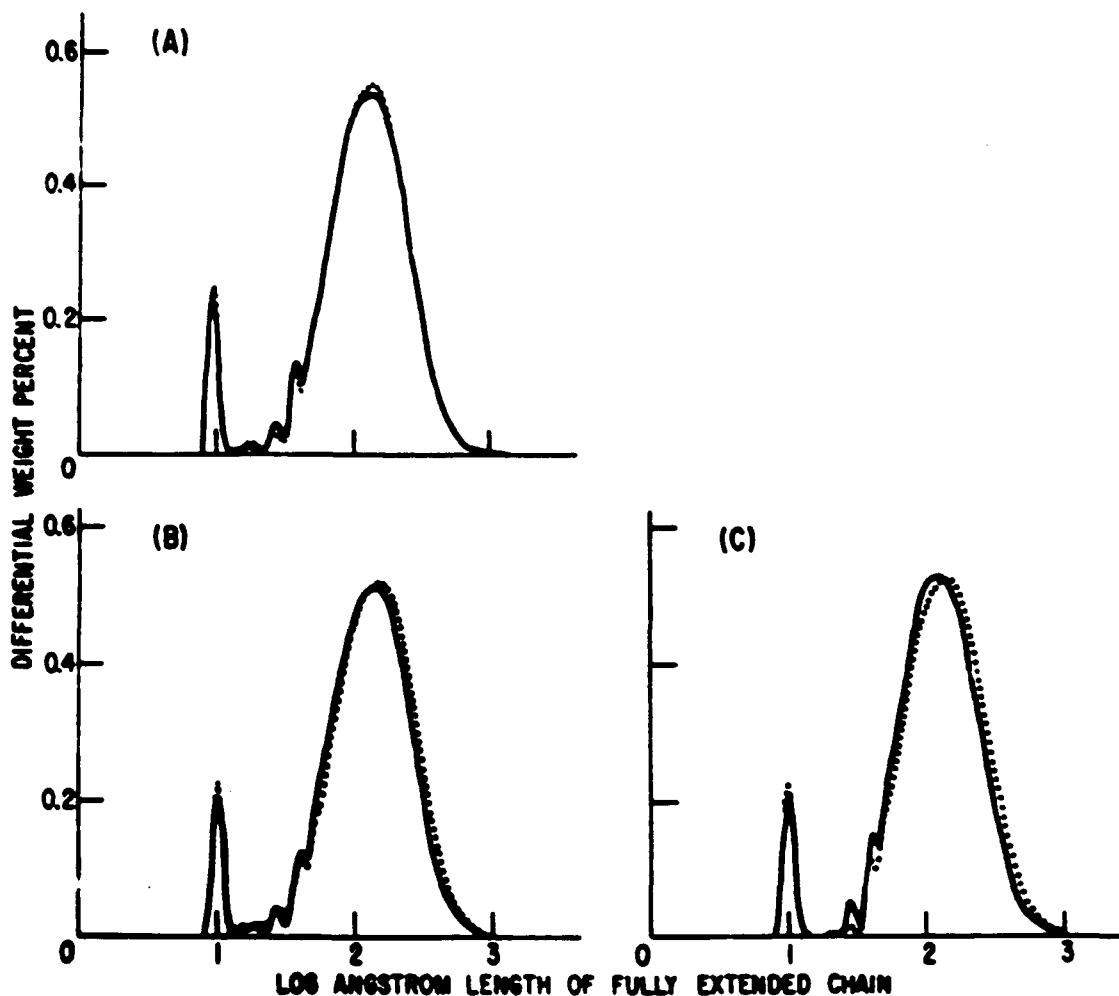
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Figure 8. ALCOHOLYSIS STABILITY of HOT STANNOUS CHLORIDE DIHYDRATE-CATALYSED, WATER WASHED ESTOL B (M.W. 1972) BLENDS with 2.0 MOLES of 1,4-BDO. EFFECT of ADDED STANNOUS CHLORIDE DIHYDRATE on BLEND MWD.



(A) NO ADDED $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, AGED at 93°C (Exp. 7745-74-18-8), (B) NO ADDED $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, AGED at 100°C (Exp. 7745-74-58-1), (C) 100 ppm $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, AGED at 100°C (Exp. 7745-74-58-2).

..... ORIGINAL MWD

———— MWD after 4 WEEKS of THERMAL AGING

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Figure 8 (C) (Blend 7745-74-58-2) shows the effect of a high level (100 ppm) of $\text{SnCl}_4 \cdot 2\text{H}_2\text{O}$ which was added to the foregoing blend. The normalised GPC curves show slightly greater changes after 4 wk./100°C. heat aging due to the added stannous chloride than were produced in the control blends without the added catalyst. But, even so, the $\bar{M}_w$ changes are minor, as can be seen in Figure 8 and Table VII data: before exposure the $\bar{M}_w$ value was 160Å and after exposure 140Å (87% retention of the original value).

B. Changes in Blend 1,4-BDO Content (by GC)

Table VIII shows changes in 1,4-BDO content and $\bar{M}_w$ values in the two blends, with and without added $\text{SnCl}_4 \cdot 2\text{H}_2\text{O}$, after heat aging. The data on 1,4-BDO level retention show similar retention of the original 1,4-BDO content (about 80%) after 4 weeks storage at 100°C. for the two blends. The loss in 1,4-BDO content for the blend containing 100 ppm of $\text{SnCl}_4 \cdot 2\text{H}_2\text{O}$ appears to be slightly greater than for the control blend, but the differences are within experimental error.

These data show that some alcoholysis takes place in the blends at 93° and 100°C. even in the absence of an active catalyst for esterification or urethane formation. The addition of 100 ppm of $\text{SnCl}_4 \cdot 2\text{H}_2\text{O}$ has only a marginal effect on the alcoholysis stability of the blends.

TABLE VIII

Changes in 1,4-BDO Content and MWD of
 $\text{SnCl}_4 \cdot 2\text{H}_2\text{O}$ -Catalyzed and Water Washed
Estol B in Blends with 1,4-BDO.
With and Without Added $\text{SnCl}_4 \cdot 2\text{H}_2\text{O}$,
100°C. Heat Aging

7745-75 $\text{SnCl}_4 \cdot 2\text{H}_2\text{O}$ (ppm)	58-1 0		58-2 100	
	1,4-BDO	$\bar{M}_w, \text{Å}$	1,4-BDO	$\bar{M}_w, \text{Å}$
Original	10.0	158	10.3	160
After 1 wk. at 100°C.	7.5 (75)		8.4 (81)	
" 2 wks. "	9.0 (90)		8.6 (83)	
" 3 wks. "	9.6 (96)		9.4 (91)	
" 4 wks. "	7.9 (79)	147 (93)	7.9 (77)	140 (87)

Blends made from Estol B, M. W. 1972 (Sec. 11B) with 2.0 moles of 1,4-BDO

Numbers in parentheses indicate percent retention of original value

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2. Heat Stability of Blends Made with Unwashed Estol B.

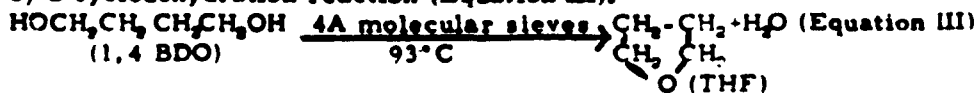
To determine the effect of stannous chloride polyesterification catalyst, residual in blends of 1,4 BDO with unwashed Estol B, on 93°C alcoholysis stability, the following experiment was run. Estol B was prepared using 65 ppm of $\text{SnCl}_4 \cdot 2\text{H}_2\text{O}$ catalyst. After preparation the untreated polyester, (Sec. I ID; MW, 1631; A. N., 0.2) was blended with two moles of two lots of 1,4-BDO containing different amounts of water. Blend 2 was made with distilled 1,4-BDO (Sec. I 2B) and contained 161 ppm water. Blend 5 was made with Production 1,4-BDO and contained 266 ppm water. Blend 1 was made with distilled 1,4-BDO and in addition contained 17% (weight) of 4A molecular sieves, to assure a completely dry system.

A. Changes in Blend Molecular Weight Distribution (GPC) and in Blend 1,4-Butanediol Content (GC).

The results appear in Table 9 and in Figure 9 (A, B, C). They show that (A) and (B) (blends contain 161 and 266 ppm of water, respectively) were quite stable during 4 weeks/93°C retaining about 80% (A) of their original 1,4-BDO content and about 85% (B) of their original blend $\bar{M}_w$ values. These are about the same values as were obtained with blends of 1,4-BDO with water-washed, stannous chloride catalyzed Estol B. It is possible that the small amount of water in the blend hydrolyzed the stannous chloride to the inactive, insoluble basic chloride, or that the stannous chloride itself is a poor catalyst for polyester alcoholysis as was suggested by blend 7745-74-58-2 stability (Figure 8 (C) and Table 8).

B. The Special Case of Blend 1: Conversion of 1,4-BDO to Tetrahydrofuran (THF) by Molecular Sieves.

The case in Figure 9 (C) whose blend contained added molecular sieves is special and most interesting. Here a substantial decrease in blend 1,4-BDO content on heat aging occurred: only 11% of the original 1,4-BDO amount remained after 4 weeks/93°C. This large loss in blend 1,4-BDO content is clearly apparent in the normalized GPC curve of the blend (Figure 9C). But it was surprising to find that the $\bar{M}_w$ value of the blend remained remarkably constant during the aging period, actually increasing slightly during the last two weeks of aging. These findings suggested that much of the 1,4-BDO content of the blend had disappeared by a mechanism different than Estol B alcoholysis. We are certain that the molecular sieves converted most of the lost 1,4-BDO to the very volatile tetrahydrofuran (THF) during the heat aging by a cyclodehydration reaction (Equation III).



For the presence of a strong THF odor in the freshly opened bottles of aged blends was easily detected. THF odor was absent in all of the other aged blends which contained no molecular sieves. On the basis of this discovery an Invention Record proposing the manufacture of tetrahydrofurane via molecular sieves has been filed (8).

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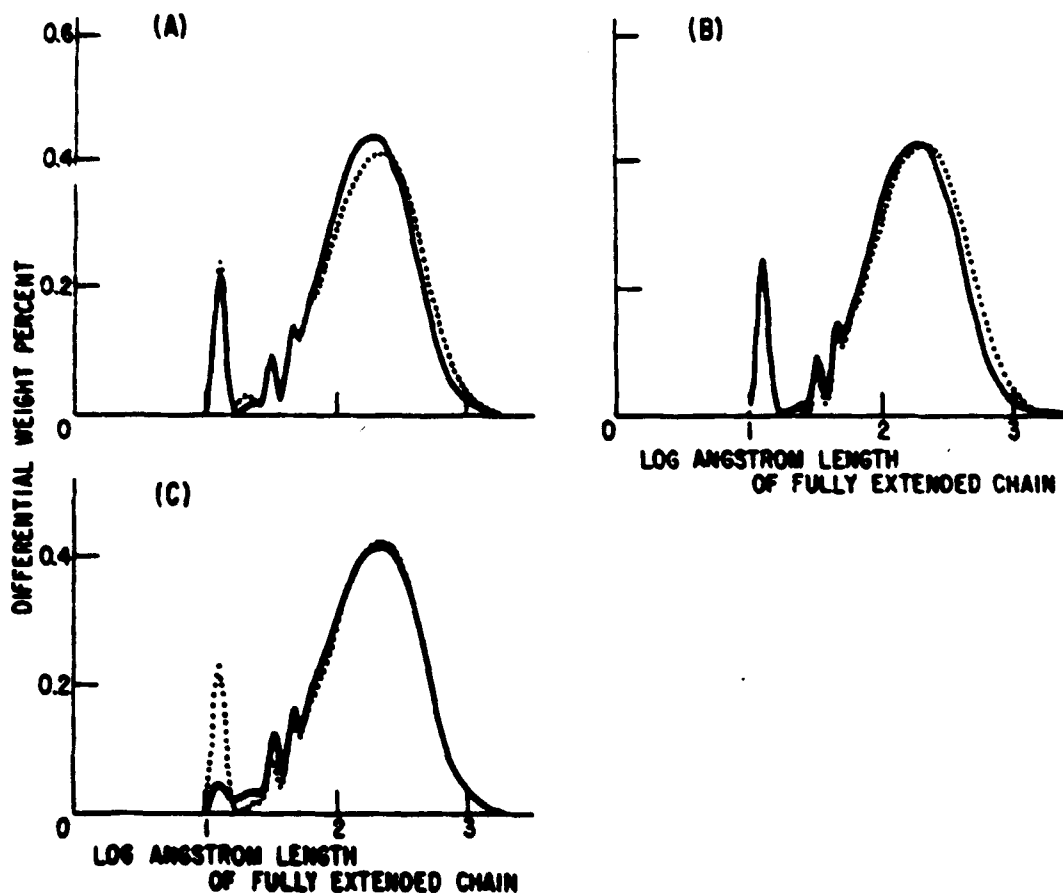
TABLE IX

Changes in 1,4-BDO Content and MWD of Estol B/1,4-BDO Blends Made from Unwashed, 65 ppm Stannous Chloride-Catalyzed Estol B on 93°C Heat Aging. Effect of Molecular Sieves.

7745-75-74 4A Mol. sieves (wt. %) Water in Blend (ppm)	1		2		5	
	17	0	161	0	266	0
	1,4-BDO (%)	1,4-BDO (%)	1,4-BDO (%)	1,4-BDO (%)	1,4-BDO (%)	1,4-BDO (%)
Original	10.4	6.6 (63)	4.1 (39)	2.0 (19)	1.1 (11)	10.4
After 1 week at 93°C	6.6 (63)	4.1 (39)	2.0 (19)	1.1 (11)	10.4	6.6 (63)
After 2 weeks at 93°C	4.1 (39)	2.0 (19)	1.1 (11)	10.4	6.6 (63)	4.1 (39)
After 3 weeks at 93°C	2.0 (19)	1.1 (11)	10.4	6.6 (63)	4.1 (39)	2.0 (19)
After 4 weeks at 93°C	1.1 (11)	10.4	6.6 (63)	4.1 (39)	2.0 (19)	1.1 (11)
	M _w , Å	M _w , Å	M _w , Å	M _w , Å	M _w , Å	M _w , Å
	219	216 (99)	201 (92)	242 (110)	227 (104)	219
	223	211 (95)	197 (88)	208 (89)	201 (86)	223

All blends made from Estol B (M. W. 1631) and 2.0 moles of 1,4-BDO. Numbers in parentheses indicate percent retention of original value.

Figure 9. MWD CHANGES in ESTOL 9/1,4-BDO BLENDS MADE from UNWASHED, STANNOUS CHLORIDE CATALYSED (65 ppm) ESTOL B on 93°C HEAT AGING.



ALL BLENDS MADE from ESTOL B (M.W. 1631) and 2.0 moles 1,4-BDO.

(A) BLEND CONTAINS 161 ppm WATER (Exp. 7745-75-74-2), (B) BLEND CONTAINS 226 ppm WATER (Exp. 7746-75-74-3), (C) BLEND CONTAINS 17% 4A MOLECULAR SIEVES (Exp. 7746-75-74-1).

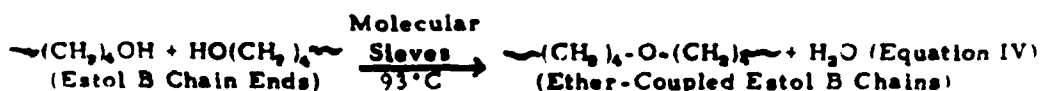
..... ORIGINAL MWD
 ——— MWD after 4 WEEKS at 93°C

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The decreasing amount of 1,4-BDO in the blend containing the molecular sieves must be the cause for the extraordinary stability of Mw during the aging period. There is also the very reasonable possibility that the observed increase in Mw is in fact real and due to the dehydro-coupling of hydroxyl terminated polyester chains. The coupling would take place between two Estol B terminal hydroxyl groups through a linear rather than a cyclodehydration reaction, which would be facilitated by the molecular sieves, with the formation of an ether linkage (Equation IV).



3. Effect of Stannous Chloride on Estane 5701.

A. Polymerization (Brabender Plasticorder Reactor, 220°C NPT).

I found that unchanged stannous chloride dihydrate is also an effective urethane polymerization catalyst, and has about the same effectiveness as stannous octoate. This can be seen in the results of Figure 10. The same Estol B (Sec. I 1G) was used in all three polymerizations of Figure 10 but the 1,4-butanediol and MDI lots varied: Run 7741-74-429 involved reactant lots 2B and 3C Run 7741-74-108, 2C and 3D; and Run 7741-74-106, 2C and 3D.

Figure 10 results show that the Brabender Plasticorder Reactor (BPR) torque-time curve for the 220°C NPT, random melt, Estane 5701 polymerization catalyzed with 65 ppm $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (429) is practically superimposable on the curve for the same polymerization catalyzed with 50 ppm of stannous octoate (108). After in situ shortstopping both polymerizations with the same amount of 1-propanol, polymerizate torque loss was the same for both.

Figure 10 data also show that the uncatalyzed control polymerization (106) was considerably slower.

The effect of residual stannous chloride left in Estol B after the esterification reaction on the polymerization rate was evaluated less quantitatively in a beaker preparation (7745-75-112) using unwashed Estol B (M. W. 1631 that had been made with 65 ppm stannous chloride dihydrate (polyesterification catalyst) (Sec. I 1D). Moderate catalytic activity was noticed: the reaction mixture could be stirred for 1 minute before it became too viscous. This should be compared with the customary two minutes stirring time for Estane 5701 polymerizations involving water-extracted (deactivated) Estol B.

B. Polymer Original Properties and Environmental Resistance.

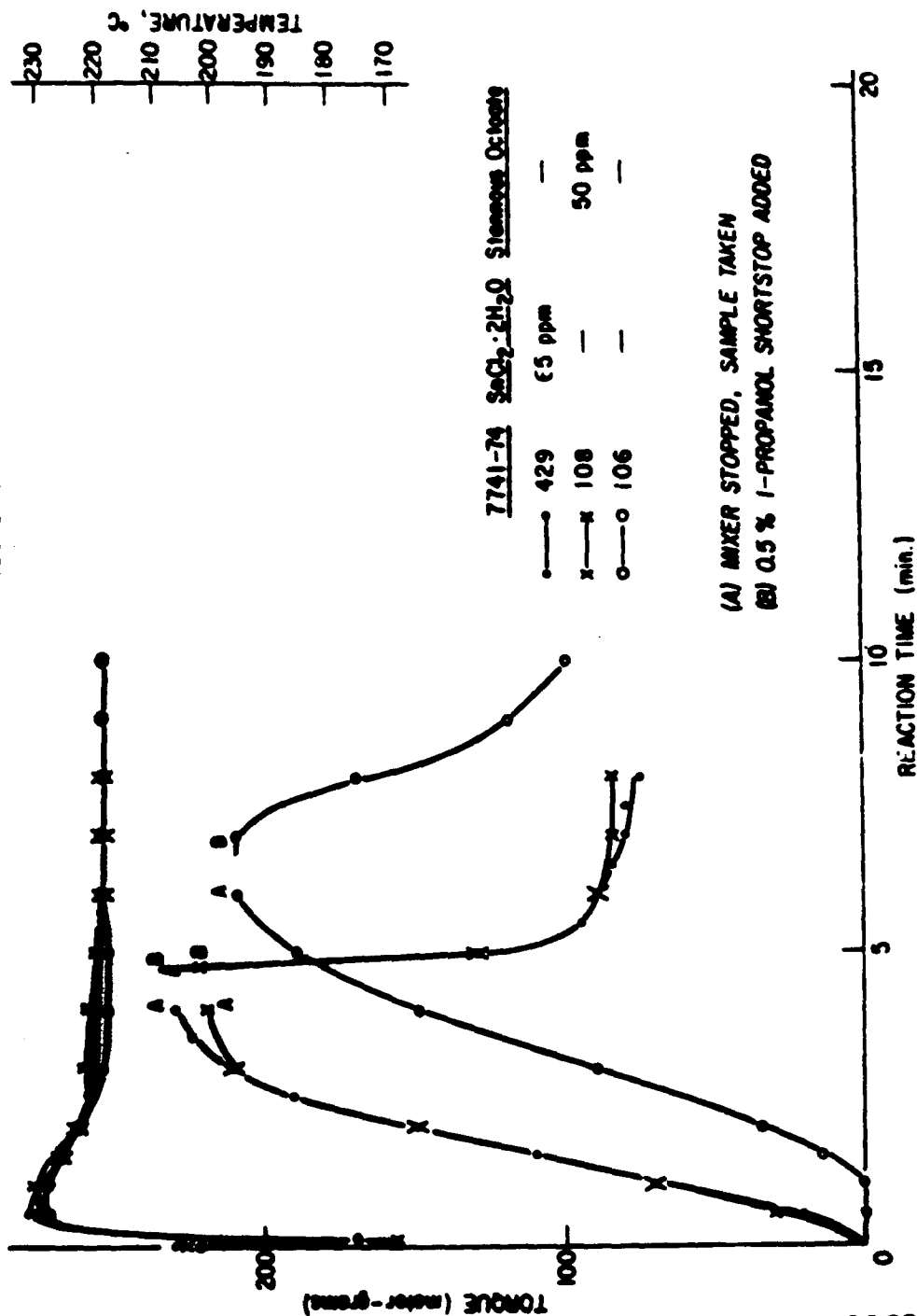
Environmental aging characteristics of Estane 5701 containing stannous chloride were reported earlier (3A), but the earlier report did not contain a

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Figure 10. EFFECT of STANNOUS CHLORIDE DIHYDRATE and STANNOUS OCTOATE on the POLYMERIZATION RATE of ESTANE 5701 at 220°C NPT.



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complete set of data. The complete study is reported now in the following section.

All four polymers in this study were made from the same 1,4-butanediol (Sec. I 2B) and MDI (See I 3E) lots but the Estol B lots were different. Polymer 7745-75-112 was made from unwashed, stannous chloride-catalyzed Estol B (M. W. 1631, Sec. I 1D). The molecular weight of this polyester is higher than is normally used in the preparation of Estane 5701, but the measured physical properties of the derived polymer were practically the same as those of Estane 5701.

Polymers 7745-75-113, 114, and 115 were all made from the same stannous chloride-catalyzed, water washed Estol B (M. W. 1184, Sec. I 1E). Polymer 113, which is the control polymer, contained no added (supplementary) stannous chloride catalyst. Polymer 114 contained 65 ppm of supplementary $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ which was added to the polyol blend before the polymerization. And, 130 ppm of supplementary $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ was added to the polymer 115 charge before the polymerization.

The data for the polyurethane original and aged properties are shown in Table 10. Considering the polymer original properties the uncatalyzed control polymer (113) is seen to have lower DSV, less gel, and a lower T_g value than the catalyzed polymers. Thus, the uncatalyzed polymer achieved a lower final molecular weight.

The relatively low DSV, T_g and tensile strength values of catalyzed polymer 115 are believed to be somehow due to the large amount (130 ppm) of stannous chloride catalyst contained in the polyurethane which also appears to have reduced thermal stability, since considerable bubbling was observed when it was subsequently molded at 185°C. No bubbling was observed in Polymers 113 and 114 when molded at the same temperature. Polymer 115 could be molded without difficulty at 175°C.

The faint yellow original color of polymer 112 (residual $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$) is slightly deeper than that of the control polymer, 113. Polymers 114 and 115 (65 ppm and 130 ppm supplementary ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, respectively) were of about the same color, and both slightly darker than polymer 112.

Table 10 data show that neither residual nor supplementary $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ at the indicated levels adversely affect Estane 5701 mechanical properties nor color stability to the limits of the dry carbon arc Weatherometer exposure (154 hours).

Hydrolysis tests (9 weeks immersion in 70°C water) show that neither residual nor supplementary (65 ppm) $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ had any adverse effect on polyurethane physical properties on color or water aging. But the data do show that 130 ppm of supplementary $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ had a slight adverse effect on hydrolysis resistance (stress-strain property retention and color).

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TABLE I
Environmental Resistance of Esters 5701 Containing Various Amounts of Stannous Chloride Dihydrate.

7700-75 Exptl. B, Mol. Wt., Treatment 5 wt.-% ZnO added before polymerization Days T _g /T _g , °C	112			113			114			115		
	1631 Unetched ZnO, 75, gal -20/150			1104, water washed ZnO, 75, gal -20/150			1104, water washed ZnO, 65 ppm 1.04, 17% gal -12/152			1104, water washed ZnO, 65 ppm 1.51, 4% gal -14/138		
	Total Str. gal	300% M gal	Elong. %	Total Str. gal	300% M gal	Elong. %	Total Str. gal	300% M gal	Elong. %	Total Str. gal	300% M gal	Elong. %
Originals, 25 mil ^b	6000	1300	495	9200	1400	500	8100	1500	400	7400	1300	515
After 48 hrs. in C. A. W. O ^c	3100 (39)	1200 (92)	415 (84)	2300 (25)	1400 (100)	300 (77)	2300 (28)	1400 (93)	300 (79)	2100 (24)	1300 (100)	395 (77)
After 80 hrs. in C. A. W. O ^c	2400 (30)	1100 (85)	420 (85)	1400 (17)	1200 (86)	350 (79)	1300 (16)	1200 (80)	325 (68)	1200 (16)	1200 (92)	290 (64)
After 154 hrs. in C. A. W. O ^c	1400 (20)	1100 (80)	365 (74)	1100 (12)	-	275 (55)	900 (12)	-	235 (49)	900 (12)	-	150 (29)
Originals, 25 mil ^b	6000	1300	495	9200	1400	500	8100	1500	400	7400	1300	515
After 1 wk. in 70°C water	7000 (92)	1400 (100)	535 (100)	7000 (79)	1400 (107)	530 (106)	7000 (86)	1400 (94)	545 (113)	6800 (92)	1400 (100)	500 (112)
After 2 wk. in 70°C water	8200 (108)	1400 (100)	575 (116)	7500 (81)	1400 (106)	575 (115)	7200 (89)	1400 (94)	580 (121)	6700 (94)	1500 (115)	540 (105)
After 3 wk. in 70°C water	6700 (84)	1300 (100)	640 (129)	6100 (64)	1300 (93)	610 (122)	6000 (74)	1200 (80)	620 (129)	4800 (65)	1200 (92)	600 (132)
After 6 wk. in 70°C water	1300 (16)	700 (54)	650 (130)	1300 (14)	800 (57)	675 (134)	1200 (15)	800 (53)	715 (150)	550 (7)	-	280 (44)
After 9 wk. in 70°C water	210 (3)	-	10 (2)	250 (3)	-	35 (7)	170 (2)	-	20 (4)	Break before testing	-	-
Originals, 75 mil ^b	6000	1100	500	7400	1100	510	7000	1100	405	6900	1100	515
After 3 days at 140°C	5400 (82)	770 (70)	600 (120)	7400 (100)	1100 (100)	505 (99)	7400 (97)	1100 (100)	515 (101)	5610 (81)	910 (85)	1100
After 7 days at 140°C	4700 (69)	600 (42)	635 (131)	6800 (93)	1100 (100)	515 (103)	6400 (87)	870 (79)	540 (100)	4300 (62)	900 (82)	1100

(a) 0.400g/d. TMS + 0.07% n-Pt.

(b) 1/8" diameter.

(c) dry carbon arc Weatherometer.

Numbers in parentheses indicate percent retention of original value.

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Oven aging (7 days/140°C/air) results show that the residual stannous chloride catalyst in Polymer 112 (made from unwashed Estol B) and the 130 ppm of supplementary stannous chloride in polymer 115 reduced the mechanical property retention of Estane 5701. Tensile strength retention was about 93% for the control polymer, 113, made from washed Estol B (but this seems high since other control polymers have retained only 87% and 67% of their original tensile strengths after the same exposure) vs. about 65% retention of the original tensile strength in the catalyzed polymers, 112 and 115. However, Polymer 114, containing 65 ppm of supplementary stannous chloride unexpectedly showed only minor reduction in mechanical property level on oven aging with respect to the control polymer. So the effect of stannous chloride on tensile strength retention is not entirely clear.

All three Estane 5701 polymers containing stannous chloride discolored more than the control polymer on oven aging. Polymers 114 and 115, containing supplementary stannous chloride, discolored more than polymer 112 which contained only residual stannous chloride catalyst.

(1) Solution of the Oven Aging "Brown Speck" Mystery.

One feature of the above sample discoloration on oven aging was the development of a coarse pattern of small brown specks in the exposed samples which became more pronounced with increasing oven aging time. The unsuspected cause of this phenomenon and solution of the mystery has been reported (9). Excerpts from that report are included here since the investigation was an integral part of the present study.

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Our "detective story" unfolded like this. We have found that thermally induced alcoholysis of titanium-catalyzed Estol B in stored blends with 1,4-butanediol can be corrected by the addition of minor titanium chelator, or by substituting stannous chloride polyesterification catalyst for the standard Production tetra (2-ethylhexyl) titanate catalyst. In the course of studying this substitution we explored the environmental stability of Estane polyurethanes prepared from stannous chloride-catalyzed Estol B. One of the Estane exposures was our standard 140°C heat aging test in a circulating air oven. As usual, brown specks scattered throughout the compression molded test sample developed in the Estane 5701 molded sheet. Since Research has long used only $\text{SnCl}_4 \cdot 2\text{H}_2\text{O}$ as Estol polyesterification catalyst we suspected that the brown specks might represent small, localized concentrations of insolubilized tin catalyst residue from the Estol B, and set out to determine if this were true.

First of all our laboratory Bausch and Lomb stereomicroscope showed interesting detail in the brown specks which we observed and recorded with our camera attachment. Each speck proved to consist of a small, very dark, opaque, dense core surrounded by a relatively large sphere of diffuse brown color. Often there was a distinct separation between the core and its surrounding colored zone. Sometimes the separated diffuse color zone was a hemisphere (above/below?) the core.

Next, we asked Peg Mack (D/8510) to focus on the brown specks with the BRDC scanning electron microscope and, applying the energy dispersive x-ray analysis capability of this instrument, to tell us what elements comprise the brown specks. We anticipated that Peg's report would be tin and (possibly) chlorine. But she reported only chlorine, and in appreciable amount! We asked her to look again, searching more carefully for the metal cation that went with the chlorine. Still only chlorine! Review of possible alternative chlorine sources suggested that PVC might be the culprit. But no PVC had been added to the Estane, and the Estane had not been exposed to PVC (we thought). So how did it get in the polyurethane?

To shorten the story a bit- we routinely sheet out our Estane polymers on a mill prior to compression molding samples for testing purposes. We used to have the milling done in the BRDC rubber mill room but quit this practice due to frequent oil and carbon black contamination of our Estane stocks, and to patronize our BRDC

Plastics Department milling facility. But unknown to us, PVC contamination of our Estane stocks during milling on our plastics mill apparently replaced the oil/carbon black contamination from the rubber mill. And this unsuspected PVC contamination may have influenced Estane stability/stabilization tests in past studies. (Fortunately, P.C. Kelley's solution mixing technique in his study of Estane UV color stability largely avoided Estane milling and thus such PVC contamination). Subsequent trial of several special precautions showed that while PVC contamination can be somewhat reduced in our plastics mill operation it is still present and likely will remain so as long as PVC is processed on this mill.

We have not directly proven that the offensive Estane brown specks are due to PVC contaminant by excising and characterizing the tiny cores. But the following experiments which I performed leaves no doubt in our minds that the brown specks are actually due to PVC dust which is somehow picked up by Estane during its milling on the BRDC plastics mill.

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(A) Experiments With Estane 5701 Prepared from Lab $\text{SnCl}_4 \cdot 2\text{H}_2\text{O}$ - Catalyzed Estol B.
Estane 5701 (7741-75-436) was prepared in the Brabender Plasticorder Reactor (BPR) using Estol B made with 98 ppm $\text{SnCl}_4 \cdot \text{H}_2\text{O}$ calculated on the final polyester weight. Most (A) of the polyurethane was subsequently milled on our plastics mill, but a small sample (B) was left unmilled. Then both (A) & (B) were compression molded as 25 mil thick sheets under the same conditions and the molded sheets were oven aged for 3 days at 140°C in air.

Inspection of the oven aged samples showed (A) (milled) to be brown in color and to contain many of the familiar brown specks. But (B) (unmilled) which was distinctly lighter in overall color, was essentially free of any brown specks.

So I concluded that the milling operation caused the problem.

(B) Experiments with Estane 5701 Production Lot #649, 338 (from titanium catalyzed Estol B).

Reference (9) contains a set of color photographs keyed below which appear in Ref. (9) Distribution copies (E. G. Schwaegerle, R. R. Bloor, F. T. Boron, D. D. Dittmer-R. L. Markley, H. E. Gaylor, C. H. Lufter-R. W. Smith-M. Mack-F. S. Myers, D. E. Ley, L. E. Hewitt, C. S. Schollenberger, R&D Files (BRDC) (7742-76).

- Sample 1 - Estane compression molded ^a without milling.
Sample 2- Estane compression molded ^a without milling, then heat aged. ^b
Sample 3- Estane milled on BRDC plastics mill, then molded, then heat aged. ^b
Sample 4- Estane mixed with 0.25 phr PVC^c on BRDC plastics mill, molded, heat aged. ^{b, c}
Sample 5- Estane mixed with 0.50 phr PVC^c on BRDC plastics mill, molded, heat aged. ^{b, c}
Sample 6- Estane mixed with 1.00 phr PVC^c on BRDC plastics mill, molded, heat aged. ^{b, c}

- (a): 25 mil thick
(b): Six days/140°C/air
(c): 103 EPF76, (Lot 22798-1)

(C) Experiment with Estane 5740 x 430. A section of Estane 5740 x 430 extruded tubing obtained from Dale Hall (ALTC) was heated for several days in the 140°C circulating air oven. It turned a uniform brown, like sample 2 in the photo, but did not develop brown specks.

The adverse effect of chlorine/chloride on Estane color stability is recognized, and has been studied (F. D. Stewart, Research Report, "The Effect of Chloride on Estane Color," Project 2074-70, Aug. 10, 1970). The present investigation seems to further confirm this. Apparently, in the case of PVC the culprit is hydrogen chloride, thermally cleaved from the PVC contaminant during the oven aging of the Estane host sample.

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REFERENCES

(1) Research Report, "Method of Determining the Free BDO (1,4-Butanediol) Content of Estol B (Hydroxy Poly (Tetramethylene Adipate) and Its Blends With BDO by Vacuum Distillation. The Stability of Estol B-BDO Blends to Heat. The Detection of Tetramethylene Adipate Monomer in Estol B.", K. Dinbergs, Project 111-43, Sept. 5, 1961.

(2) B. F. Goodrich Chemical Company Technical Report, "Backbone M. W. Analysis on Estol Blends", Author, J. B. Haehn, Requested by, J. W. Hockenberry, Avon Lake General Chemical Plant, November 13, 1973.

(3) A. Research I. O. C. "Environmental Aging Characteristics of Estane 5701 Containing Stannous Chloride or Stannous Octoate Catalysts," K. Dinbergs to C. S. Schollenberger, Project 7745-75, July 24, 1975.

B. Avon Lake Technical Center I. O. C. "Testing Program for Improved Storage Stability of Estol Blends," John A. Holloway to R. R. Bloor, Dec. 18, 1974.

C. Research I. O. C., "1,4-Butanediol Determination by Gas Chromatography in Estol B/1,4-Butanediol Blends Prepared and Heat Aged at Avon Lake," K. Dinbergs to C. S. Schollenberger, Project 7745-75, May 13, 1975.

D. B. F. Goodrich Chemical Company Technical Report "Evaluation of Chelators and Catalyst in Estol Stability," Author of J. B. Haehn Requested by J. A. Holloway, ALTC, June 9, 1975.

E. Monthly Status Reports (Estane Research) C. S. Schollenberger to R. R. Bloor Projects 7745-74, 75, March 1974 to December 1975.

F. B. F. Goodrich Chemical Company Technical Report, "Evaluation of Stannous Chloride in Estol Blends", Author, J. B. Haehn, Requested by E. G. Kolycheck, Avon Lake Technical Center, November 4, 1975.

G. B. F. Goodrich Chemical Company Technical Report, "Effect of Storage Time and Temperature on the Stability of Estol 5740 x 610 Blend from Stannous Chloride Catalyzed Polyester", E. G. Kolycheck, Avon Lake Technical Center, November 10, 1975.

(4) Thermoplastic Polyurethane Melt Polymerization Studies in the Brabender Plasticorder.

II. Estane 5701: Further Investigation of Shortstop, Catalyst, and Temperature Effects. K. Dinbergs, Project 7741-74, 75, August 14, 1975.

(5) U.S. Patent 3,057,824, "Tin Salts as Catalysts in Forming Polyesters," Oct. 9, 1962, L. E. LeBras and D. F. Stahr Assignors to Pittsburgh Plate Glass Co.

(6) Research Report, "Low Acid Number Poly (Tetramethylene Adipate) Glycol (Estol B), F. D. Stewart, Project 124-48, Oct. 25, 1966.

(7) U.S. Patent 3,463,758, "Hydrolysis Resistant Poly (Ester Urethanes)," Aug. 26, 1969, F. D. Stewart, Assignor to the B. F. Goodrich Company.

(8) Invention Record #4413N (BFGCC), "Preparation of Tetrahydrofuran", K. Dinbergs, May 22, 1975. (Placed in SECRET category)

(9) Research I. O. C., "Contamination of Estane With PVC", K. Dinbergs to C. S. Schollenberger, Project 7742-76, Feb. 10, 1976.

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