

## An Investigation of Factors Relating to the Exudation of Polyester Plasticizers from Poly(vinyl chloride)

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### Synopsis

Poly(vinyl chloride) (PVC) was plasticized with a given polyester. The resulting exudate under humid conditions was qualitatively analyzed by GPC and GLC. The exudate was found to have a greater concentration of low molecular weight species than the original polyester. Further, a much higher hydroxyl group concentration was present. The described polyester was also fractionated and characterization studies were performed. The relative migratory aptitude in PVC of these moieties was studied under humid conditions. The fraction with the greatest concentration of low molecular weight species and the highest hydroxyl concentration was exuded first.

### INTRODUCTION

Polyester plasticizers were introduced to the vinyl industry in the early 1940's.<sup>1,2</sup> Because their average molecular weights are much higher than monomeric plasticizers, they exhibit lower vapor pressures and slower rates of diffusion within the polymer matrix. These factors contribute<sup>3,4</sup> to giving polyester plasticizers high residence characteristics in vinyl resins and consequential high commercial acceptability as "permanent" plasticizers.

Under adverse conditions, such as high humidity, "permanent" plasticizers do occasionally show a tendency to migrate from poly(vinyl chloride). The purpose of this paper is to present in detail the experimental endeavors that were designed to determine the nature of the above migration. A greater understanding of such migration can only lead to the development of better polyester plasticizers for poly(vinyl chloride).

A few comments about general structure-activity relationships as they pertain to polyester plasticizers is in order at this point. Countless books and articles have been written on the subject of plasticizers in general.<sup>5-8</sup> However, Boyer<sup>9,10</sup> has done an excellent job of documenting the three main interdependent factors that we seek to maximize in all plasticizers, i.e., compatibility, efficiency, and permanence. From the point of view of polyester plasticizers, we must now isolate the appropriate basic parameters which will enable us to design polymers to meet the demands of the

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above trichotomy. At this time we envisage four basic parameters to be taken into consideration in synthesizing a suitable polyester plasticizer.

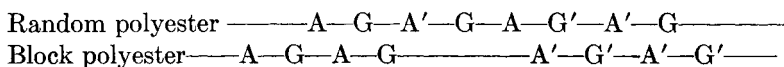
### The Reactants

The fact that there is a variance in polyester plasticizer properties with respect to its composition is certainly most obvious and is well documented.<sup>5,11-17</sup> Brice et al.<sup>11</sup> describe the effects on the properties of a series of polyesters when the dibasic acid is varied, keeping all other constituents constant. Similarly he describes the effect of varying the glycol. Parkyn et al.<sup>15</sup> have written a short review on this topic.

Polyester plasticizers can be terminated with either monohydric alcohols or monobasic acids. The choice of such agents is arbitrary but they are generally used as one means of regulating the resultant molecular weight.<sup>18</sup> Polyester plasticizers can be produced without the use of terminating agents<sup>14,19</sup> but they display different plasticizing ability and properties to those in which they are included. Work in these laboratories<sup>19</sup> has shown that different degrees of permanence, compatibility, and efficiency are experienced when an acid terminator is varied along a homologous series. These effects are easily observed by variances in tensile strengths, elongation properties, and low temperature properties of the plasticized vinyl. Differences in the rates of plasticizer exudation or migration from the vinyl stock are also evident.

### The Sequence of Reactants

It is possible to have the same constituents in a polyester but with varying molecular arrangements.<sup>17</sup> An excellent example of this is observed by comparing the resultant plasticizer properties of a random polyester made from two different glycols (G,G') and two different dibasic acids (A,A') with a block polyester made from the same ingredients.



Very little information is available with respect to the plasticizing effects of such molecular mechanics, but obviously the geometry of the molecules and the physical properties are different and so are the plasticizing properties. Unpublished work from these laboratories has indicated that, in the systems examined, block polymerization compared to analogous random polymerization leads to a deleterious effect on plasticizer properties.

### The Conditions of Polymerization

The reaction conditions for making polyesters are generally considered proprietary information except on a very general basis.<sup>15,17,18</sup> Nevertheless, a great deal of information is available in the patent literature<sup>1,2,15</sup> which will convince most chemists that the reaction conditions do have a pronounced effect upon the plasticizing properties of the final product.

The reasons for the above are manifold, but a few of the more important

considerations are as follows. If the reaction conditions are not correct, the balance of the total reactants can be disturbed by reactant losses and a different product than desired can result. Assuming the reaction is stopped too soon, a greater concentration of hydroxy or carboxy functions will be present which will alter the physical properties of the plasticizer. The basic reason for these manufacturing problems is probably partly explained by molecular weight considerations.

Excessively high temperature of reaction will lead to somewhat different products owing to degradation.

### Molecular Weight and Molecular Weight Distribution

Some information is available on the effect that the average molecular weight has upon polyester plasticizer properties. Early workers in the field of polyesters such as Leilich<sup>20</sup> and Jones and co-workers<sup>21,22</sup> forwarded concepts relating the viscosity of polyesters to efficiency, etc. Since the polyesters in question are generally linear, a relationship to molecular weight is obvious. The molecular weight has a pronounced effect upon the diffusivity constants of polymeric plasticizers within the parent polymer. This directly affects the exudation ability or permanence of the plasticizer. The vapor pressure and hence volatilization characteristic are also dependent upon molecular weight. However, in the case of polymeric plasticizers, the volatilization process is not generally an important consideration.<sup>4</sup>

The literature on polyesters in general is very adequate.<sup>15,17,23</sup> However, that dealing predominantly with oligomeric polyesters is not as replete. Valuyev and co-workers<sup>24</sup> recently published convincing evidence that oligomeric polyesters below  $\bar{M}_n \sim 3000$  do not have the most probable Flory distribution in which  $\bar{M}_w/\bar{M}_n$  is 2. They found that for such low molecular weight polyesters  $\bar{M}_w/\bar{M}_n$  is 1.2 to 2.

The polyester plasticizers commonly used in the vinyl industry tend to be oligomeric. Furthermore, because unequivalent ratios of dibasic acid to glycols, mixtures of acids, glycols, and terminating agents are used, the molecular weight distributions of polyester plasticizers tend to be even more skew in nature.

Virtually no information is available concerning the effects of molecular weight distributions and associated characteristics of oligomeric polyester on plasticizing properties. The remainder of this paper is a report on our researches in this area. Of particular interest were discernible effects on the permanence portion of "Boyer's Trichotomy." Permanence to solvent attack (other than water vapor) is not considered in this paper.

## EXPERIMENTAL

### Polyester Synthesis

A polyester was prepared from 1:4 butanediol, 1:2 propanediol, adipic acid, and dodecanoic acid. Excess hydroxyl equivalents (5%) were used.

The reaction was catalyzed by hypophosphorus acid (0.1% by wt), and hydroquinone (0.05% by wt) was used as the stabilizer. The reaction was conducted under a blanket of nitrogen at 220–230°C, and toluene was used for the azeotropic removal of water. When an acid value of 2 was reached, the polyester was stripped under reduced pressure (5–10 mm) and filtered.

### Fractionation of Polyester

A solution of polyester in acetone (33 $\frac{1}{3}$ % by wt) was added dropwise to five times its volume of vigorously stirred aqueous methanol.

In fractionation 1, the ratio (by wt) of methanol to water was 3:1. In a second fractionation of the original polyester, the ratio of methanol to water was 9:1.

The insoluble higher molecular weight fraction was drained off and stripped under reduced pressure (5–10 mm) for  $\frac{1}{2}$  hr at 100°C.

The aqueous methanol–acetone solution (containing the lower molecular weight fraction) was concentrated under reduced pressure (5–10 mm) at 50°C or less. The last traces of solvent-precipitant were removed by heating the fraction under reduced pressure (5–10 mm) for  $\frac{1}{2}$  hr at 100°C.

### Polyester Standards for Exudation Analysis

The polyesterifications were catalyzed by dibutyl tin oxide (0.1% by wt) and no toluene was used for the azeotropic removal of water. The reactions were carried out under nitrogen at 200–230°C and stopped either when the acid value fell to unity when excess diol was used or when it became constant when excess acid was used.

### Compounding of Polyester with Poly(vinyl Chloride) (PVC)

PVC resin (100 g), plasticizer (50 g), and a barium–cadmium stabilizer (2.5 g) were processed on a two-roll rubber mill for 10 min at 177°C. Twenty-mil stock was prepared and used in the exudation tests.

### Exudation Experiments

A 20-mil sheet (1 $\frac{1}{2}$ " by 2") of the polyester compounded with PVC was suspended over distilled water (50 ml) in a capped 8-ounce jar. The jar was placed in an air-circulating oven at 60°C.

The time taken for exudation to occur under given test conditions was determined by the point when a distinct greasy feeling became evident upon touching the surface of the sheet. It should be noted that exudation could occur but be insufficient to be detected by touch.

When the exudation was to be isolated and analyzed, several 20-mil sheets were left for 15–16 weeks under the previously described conditions. At that time, the water in the capped jars contained oily droplets of exudation and the sheets themselves were greasy to the touch.

The water-exudation mixture was shaken with benzene. The organic layer was separated and dried several days over anhydrous sodium sulfate. The filtered solution was then stripped below room temperature under reduced pressure (1–2 mm). A brown, oily residue was left which was found to contain 0.84% water (Karl-Fischer determination).

The greasy sheets were dipped into anhydrous acetone for 30 sec. The acetone solution was filtered and left to evaporate over a period of days at room temperature. The residual oil was dissolved in benzene and treated as described for the water-exudation mixture. A pale yellow oil was left which contained 0.36% water (Karl-Fischer determination).

### Analytical Procedures

Viscosities were determined by the bubble time procedure (ASTM D1545-63).

Acid values were determined by procedures based upon ASTM D1639-61.

Hydroxyl values were determined by procedures developed in these laboratories. They represent the number of milligrams of KOH equivalent to the hydroxyl content of 1 g of sample.

Per cent of nonvolatiles was determined by knowing the weight lost from a given weight of sample when it was placed in an air-circulating oven at 100°C for 2 hr.

The number-average molecular weight was determined at 37°C using a Mechrolab vapor pressure osmometer, Model 301A. Tetrahydrofuran was used as the solvent. Benzil was used to calibrate the apparatus.

Molecular weight distribution data were obtained by using a Waters Associates Model 200 gel permeation chromatographic unit. Tetrahydrofuran was used as the solvent. The analyses were conducted at room temperature at a flow rate through the columns of 1 ml/min.

Three types of column arrangement were used: (a) three Styragel columns in series of porosities  $10^5$ ,  $10^4$ , and 60 Ångströms, (b) five Styragel columns in series of porosity  $10^6$ ,  $10^5$ ,  $10^3$ , 250, and 60 Ångströms, (c) four Styragel columns in series of porosities 100, 100, 60, and 60 Ångströms.

Standard polystyrene samples obtained from the Pressure Chemical Company were used to calibrate the apparatus.

Gas-liquid chromatographic analysis was accomplished using a 4-ft 15% silicone column (OV-17) at 150°C and a 12-ft Carbowax 20M column at 200°C. The samples were methylated prior to GLC analysis. Standards used were methylated and nonmethylated stabilizers and methylated dodecanoic acid.

### Polyester Acetylation

Acetic anhydride was used to acetylate polyesters at 160°C for 1 hr. The mixture was then stripped under reduced pressure (5–10 mm) at 200–230°C for 3/4 hr.

## RESULTS AND DISCUSSION

## Polyester Fractionation

The analytical properties of a polyester derived from 1:4 butanediol, 1:2 propanediol, adipic acid, and dodecanoic acid are given in Table I.

TABLE I  
Analytical Properties of Polyester

Viscosity (Stokes)	17
Acid value	0.9
Hydroxyl value	17
% Nonvolatiles	99.9
Number-average MW	1430

This polyester was fractionated using an acetone-aqueous methanol system. The variation in the quantity of water present in the precipitant resulted in the production of two high and two low molecular weight fractions, each of different average molecular weight.

Table II gives the analytical properties and yields of the various fractions.

TABLE II  
Analytical Properties of Polyester Fractions

	Fractionation 1		Fractionation 2	
	High MW	Low MW	High MW	Low MW
Viscosity (Stokes)	21	6	43	7
Acid value	0.4	2.3	0.3	1.2
Hydroxyl value	11	49	6	21
Number-average MW	1380	804	1820	979
% Nonvolatile	100	99.9	100	99.9
Yield, g <sup>a</sup>	380	98	200	282

<sup>a</sup> Total isolated yield from each fractionation (starting with 500 g polyester) was 95.6% and 96.4%. Further high molecular weight material separated out from the aqueous methanol-acetone solution on standing, prior to concentrating the low molecular weight fraction. This higher molecular weight material was discarded.

TABLE III  
Average Chain Length of Original Polyester and Its Fractions

	$\bar{A}_w$	$\bar{A}_n$	$\bar{A}_w/\bar{A}_n$
Original polyester	111	67.7	1.64
Fractionation 1			
low MW	67.0	40.2	1.67
high MW	122	77.8	1.57
Fractionation 2			
low MW	80.5	50.1	1.61
high MW	147	91.9	1.60

The average chain length and molecular weight distribution of the original polyester and each fraction were all determined by gel permeation chromatography using three Styragel columns in series, of porosity  $10^5$ ,  $10^4$ ,  $60 \text{ \AA}$ ngströms. The chain length data are given in Table III; the molecular weight distributions can be deduced from Table IV.

TABLE IV  
Molecular Weight Distributions of  
Original Polyester and Its Fractions

Chain length, $\text{\AA}$	Cumulative weight %				
	Low MW fractions		Original polyester	High MW fractions	
	Fractionation 1	Fractionation 2		Fractionation 1	Fractionation 2
595	—	—	100	—	100
419	100	—	99.8	100	99.8
289	99.8	100	99.1	98.6	97.6
200	99.2	99.6	94.6	93.2	88.1
140	96.4	94.5	81.8	77.6	66.7
95	90.7	78.9	60.8	54.0	39.5
66.5	72.9	56.3	39.6	32.6	20.8
46.5	49.4	35.6	23.4	17.7	10.5
33.0	32.2	20.7	12.6	8.6	5.4
24.0	19.6	12.0	6.8	4.3	3.2
17.5	10.9	6.3	3.2	1.8	1.8
13.0	6.3	3.5	1.4	0.8	1.2
9.9	2.8	1.8	0.5	0.6	1.0
7.8	0.6	0.6	0.2	0.2	0.4

TABLE V  
Average Molecular Weights and Chain Lengths  
of Original and "Recombined" Polyesters

	$\bar{M}_n$ from VPO	$\bar{A}_w^a$	$\bar{A}_n^a$	$\bar{A}_w/\bar{A}_n^a$
Original polyester	1430	111	67.7	1.64
"Recombined" polyester	1310	112	68.4	1.64

<sup>a</sup> Determined using 3 Styragel columns in series of porosities  $10^5$ ,  $10^4$ , and  $60 \text{ \AA}$ .

Isolation of the various polyester fractions from the solvent-precipitant system could theoretically lead to undesired changes in the molecular structure of those fractions. Such changes would arise from alcoholysis, esterolysis, hydrolysis, etc.

In order to determine whether the fractionation procedure had indeed led to any significant change in the molecular structure of the fractions, the two cuts from fractionation 2 were combined in a ratio by weight of 1:1.29 (high to low molecular weight fractions). The average chain lengths as well as the number-average molecular weight of this "recombined" poly-

ester were then compared with those of the original unfractionated material (Table V).

Gel permeation chromatographic analysis of the "recombined" polyester indicated the presence of residual solvent-precipitant. When the presence of such impurities is not taken into account in calculating the average chain lengths of the "recombined" polyester, the results given in Table V are obtained. These results indicate excellent agreement between the average chain lengths of the original and "recombined" polyesters. In determining the average molecular weight by vapor pressure osmometry (VPO), the presence of such impurities cannot be ignored; thus the number-average molecular weight of the "recombined" polyester was found to be less than that of the original polyester (Table V).

Further evidence that the isolation technique leads to no side reactions is forthcoming from eq. (1). If only a separation of molecular weight species occurs on fractionation, the following equality will be true;

$$A_u = A_s \cdot W_s + A_p \cdot W_p \quad (1)$$

where  $A_u$  = wt-average chain length ( $\text{\AA}$ ) of unfractionated polyester;  $A_s$  = wt-average chain length ( $\text{\AA}$ ) of low molecular weight fraction;  $A_p$  = wt-average chain length ( $\text{\AA}$ ) of high molecular weight fraction;  $W_s$  = weight fraction of low molecular weight cut; and  $W_p$  = weight fraction of high molecular weight cut.

When the appropriate results given in Tables II and III are substituted in eq. (1), the above equality is confirmed.

TABLE VI  
Hydroxyl Concentration of Each Polyester Fraction

	$\bar{M}_n$	Hydroxyl value	Hydroxyl conc., OH groups/ molecule
Fractionation 1			
low MW	804	49	0.70
high MW	1380	11	0.27
Fractionation 2			
low MW	979	21	0.37
high MW	1820	6	0.19

Thus, it appears that the technique used to isolate the fractions from the solvent-precipitant system does not lead to changes in the molecular structure of the polyester.

Tables I and II indicate that the low molecular weight fractions have higher hydroxyl values than the original polyester. Knowing the average molecular weight of each fraction and its hydroxyl value, the hydroxyl concentration (hydroxyl groups per molecule) can be calculated. The results are given in Table VI. This table clearly indicates that the hydroxyl groups are mainly associated with the lower molecular weight species.



### Exudation

A PVC sheet plasticized with a polyester will eventually show signs of exudation if exposed to a humid atmosphere at 60°C. We are concerned with the mechanism of exudation, the retardation of this undesirable migration, and the nature of the exudate.

#### *Discussion of Factors Influencing Exudation*

Many different theories have been postulated about the mechanism of plasticization. However, it is generally accepted that there are three interdependent dynamic equilibria operating in a plasticized PVC sheet, viz. plasticizer-polymer, polymer-polymer, and plasticizer-plasticizer. The forces that contribute these interactions are summarized by Immergut and Mark.<sup>5</sup> Under hot, humid conditions the above equilibria are disturbed by the migration of water through the surface of the milled sheet (as evident by its opaqueness). Thus, new equilibria such as those involving water-polyester and water-polymer molecules are set up, thereby allowing the polyester to migrate from the polymer matrix. The main factors influencing this migration of the polyester are thus thought to be the molecular

TABLE VII  
Exudation Results

	$\bar{M}_n$	Hydroxyl conc., OH groups/ molecule	Exuded in weeks
Fractionation 1, low MW	804	0.70	1-2
Fractionation 2, low MW	979	0.37	10-11
Original polyester	1430	0.43	10-11
Fractionation 1, high MW	1380	0.27	10-11
Fractionation 2, high MW	1820	0.19	13-14

dimension and the intermolecular force to which the hydroxyl group concentration is a contributing factor. Obviously, the lower molecular weight species of a given polyester will possess faster diffusion rates. Less obvious has been the supplemental contribution of the polyester terminal functions, such as hydroxyl, toward exudation. It is not possible at this time to comment in detail on the magnitude of the effects of molecular weight versus hydroxyl concentration in polyester plasticizers. Nevertheless, we believe that the hydroxyl group concentration plays a definite role.

If one looks again at Table VI, it will be evident that the lowest molecular weight fraction also possesses the highest hydroxyl concentration. Thus, one would expect that the low molecular weight fraction (fractionation 1), when milled up with PVC, would exude quicker than any other fraction. Table VII shows supporting evidence for this prediction and for the above hypothesis.

The highest molecular weight fraction (fractionation 2) not only has far fewer low molecular weight species, but it also has a smaller hydroxyl concentration than the other fractions. Both these factors will tend to reduce its ease of exudation from a milled sheet. Thus, in a given time, less of it will be exuded and consequently clear evidence of exudation will take the longest time to appear.

#### *Retardation of Exudation*

Acetylation of a polyester reduces the level hydroxyl groups and is a well-recognized method of increasing permanence. The greater the degree of acetylation, the fewer hydroxyl groups will be present. Thus, a given polyester molecule possessing hydroxyl groups would be expected to more readily exude prior to acetylation than following it. Further, the greater the degree of acetylation, the longer it will take for an exudate to become evident. These facts have been confirmed using a polyester similar in structure to that described previously in this paper.

TABLE VIII  
Effect of Acetylation on Exudation

	Hydroxyl value	Time to exude, days	
		Slight exudation	Heavy exudation
Unacetylated polyester	27	4-7	7-9
Partially acetylated polyester	25	4-7	15-21
	20	4-7	15-21
	16	-	35-42
	7	42-50	53-58
	3	-	53-58

The results given in Table VIII indicate that as the hydroxyl level is reduced by acetylation, a progressive delay in exudation occurs. At a residual hydroxyl value of 7, the delay of exudation is virtually the same as when the polyester is completely acetylated.

So far it had been postulated that the earliest exudate is richer in low molecular weight polyester species which have a higher-than-normal hydroxyl value. This has been suspected for many years but no experimental evidence has, up to this time, been put forth; neither has the exudate been qualitatively analyzed.

#### *Analysis of an Exuded Polyester*

Two exuded samples were isolated from the described polyester. One was the exudate which had dripped off the milled sheets into the water (drip exudate); the other was exudation removed from the surface of the milled sheets by solvent extraction (off-sheet exudate). These samples were analyzed qualitatively by gel permeation chromatography and other analytical techniques in order to determine their composition.

Analysis by gel permeation chromatography involved the use of four Styragel columns in series of porosities 100, 100, 60 and 60 Ångströms. The use of such columns permitted a separation of the lowest molecular weight components present in the exuded material. Each component under the given conditions of analysis was eluted at a given count. The identity of each of the exudation components was determined by finding out what standard was also eluted at that count. Standards used were the barium-cadmium stabilizer, 1:4 butanediol, 1:2 propanediol, adipic acid, and dodecanoic acid. Further standards were mixtures derived from the interaction of the glycols with dodecanoic acid and from the interactions of a glycol with adipic acid. Since these last interactions do not yield single compounds, it was necessary to identify each of the compounds present in these standards before they could be used to identify the components present in the exudation.

#### *GPC Analysis of Reference Standards*

Interaction of the glycols with dodecanoic acid (2:1 molar ratio) would yield a product which might contain the starting material, monoester and diester. The reaction scheme is given in Figure 1.

Qualitative analysis, by gel permeation chromatography, of the reaction product from the 1:4 butanediol-dodecanoic acid (2:1 molar ratio) reaction yielded the results given in Table IX. This table indicates the counts at which various components were eluted during the gel permeation chromatographic analysis. It is clearly seen that the use of excess glycol results in the reaction product being free of dodecanoic acid. However, traces of 1:4 butanediol were detected as being eluted at 27.2 counts. The other two components detected in the reaction mixture were major ones. They are believed to be the monoester HO—1—T (Fig. 1) and the diester T—2—T (Fig. 1). From molecular weight and hydrodynamic volume considerations, one would expect the diester to be eluted first. Thus, the component eluted at 21.7 counts is believed to be the diester while the monoester is eluted at 23.5 counts.

Qualitative analysis, by gel permeation chromatography, of the reaction product for the 1:2 propanediol-dodecanoic acid (2:1 molar ratio) reaction

TABLE IX  
Qualitative Analysis by GPC of 1:4 Butanediol-Dodecanoic Acid  
Reaction Products, and Standards

Counts at which eluted	Standard eluted	Amount and time at which components of reaction products were eluted
27.2	—	minor
27.1	1:4 butanediol	—
24.6	dodecanoic acid	—
23.5	—	major
21.7	—	major

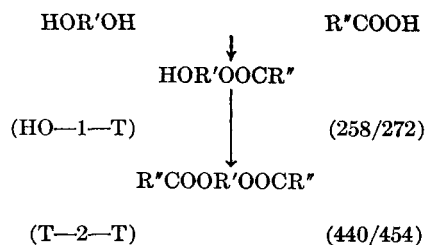


Fig. 1. Glycol-dodecanoic acid interactions: HO-1-T, molecule with a terminal hydroxyl and dodecanoic acid group and possessing only 1 ester group; T-2-T, molecule

terminated by dodecanoic acid and possessing 2 ester groups; R',  $\begin{array}{c} \text{CH}_3 \\ | \\ -\text{CH}-\text{CH}_2- \end{array}$  or  $\begin{array}{c} \text{CH}_3 \\ | \\ -\text{CH}-\text{CH}_2-\text{CH}_2- \end{array}$ ; R'', C<sub>11</sub>H<sub>23</sub>—. Numbers in parentheses refer to the molecular weight of the various compounds.

yielded the results given in Table X. Three components were present. The minor 1:2 propanediol component is readily identified as being eluted at 27.8 counts. The other two components are the major ones and are eluted at 21.8 and 23.6 counts. From what has been stated previously, it is believed that these components are the diester T-2-T (Fig. 1) and the monoester HO-1-T (Fig. 1), respectively.

The monoesters synthesized using 1:2 propanediol or 1:4 butanediol appear to be eluted at similar times, as are the corresponding diesters (Tables IX and X). This suggests that analogous esters and polyesters made from either glycol will, under the conditions of analysis, be eluted at similar times.

Interaction of the 1:2 propanediol with adipic acid (10:1 and 1:5 molar ratio) would yield various compounds, as shown by the reaction scheme given in Figure 2. Qualitative analysis, by gel permeation chromatography of the reaction products from the glycol-adipic acid interaction (Fig. 2), indicates that in both reactions the excess starting components are present.

TABLE X  
Qualitative Analysis by GPC of 1:2 Propanediol-  
Dodecanoic Acid Reaction Products, and Standards

Counts at which eluted	Standard eluted	Amount and time at which components of reaction product were eluted
27.9	1:2 propanediol	—
27.8	—	minor
24.6	dodecanoic acid	—
23.6	—	major
21.8	—	major

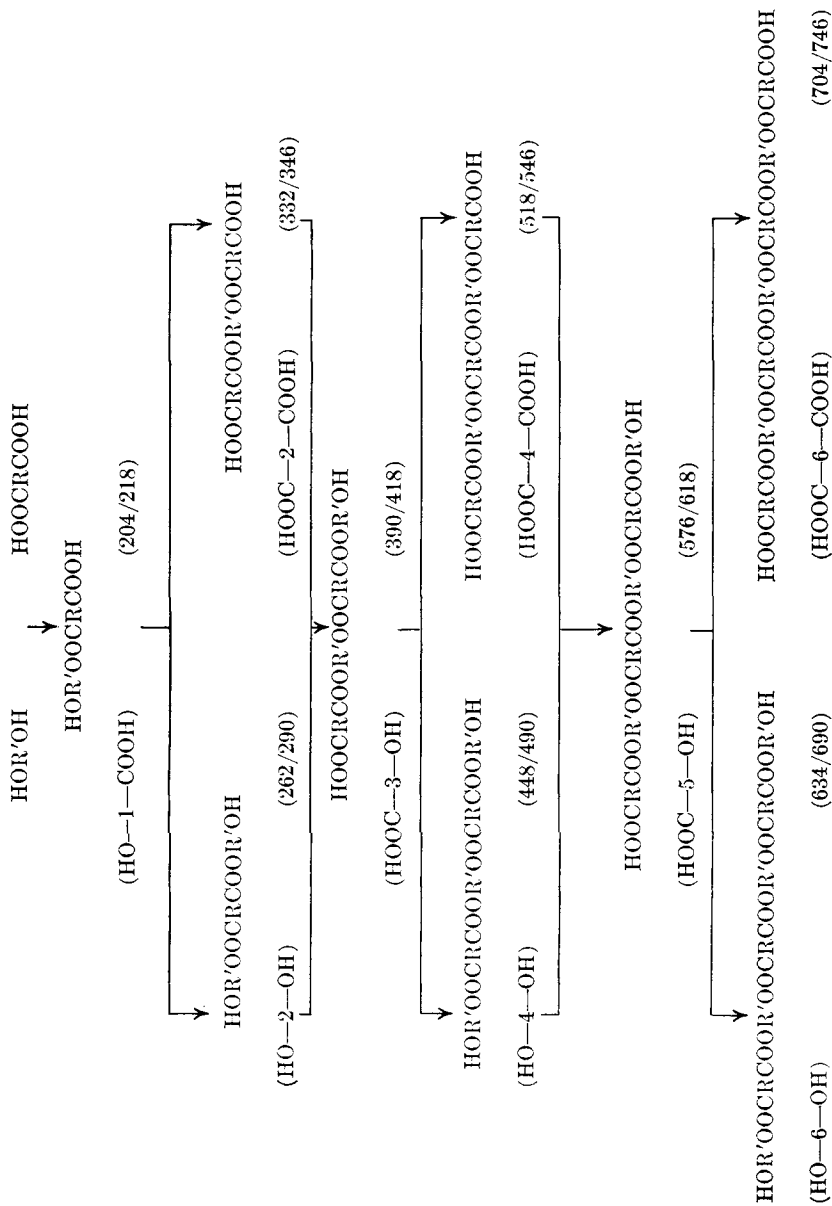


Fig. 2. Glycol-adipic acid interactions:  $\text{HOOC}-6-\text{OH}$ , molecule terminated by a hydroxyl and carboxyl group and possessing 6 ester groups;  $\text{R}'$ ,  $\text{CH}_3$  or  $-\text{CH}-\text{CH}_2-\text{CH}_2-$ ;  $\text{R}$ ,  $-(\text{CH}_2)_r-$ . Numbers in parentheses refer to the molecular weight of the various components.

TABLE XI  
Qualitative Analysis by GPC of 1:2 Propanediol-  
Adipic Acid Reaction Products (10:1), and Standards

Counts at which eluted	Standard eluted	Amount and time at which components of reaction product were eluted
27.9	1:2 propanediol	—
27.7	—	major
25.2	adipic acid	—
23.6	—	major
21.7	—	minor
20.5	—	minor

TABLE XII  
Qualitative Analysis by GPC of 1:2 Propanediol-  
Adipic Acid Reaction Products (1:5), and Standards

Counts at which eluted	Standard eluted	Amount and time at which components of reaction product were eluted
25.3	—	major
25.2	adipic acid	—
22.6	—	major
21.2	—	minor

Tables XI and XII indicate that the use of excess 1:2 propanediol results in the appearance of three other low molecular weight components in the reaction mixture, while excess adipic acid produces only two other low molecular weight components. Further, none of the components present in the two reaction mixtures is eluted at similar times. This indicates that the components present in the two reaction mixtures differ from each other.

The use of an excess of glycol or acid suggests that the final reaction product will contain little if any esters of the form  $\text{HO}-x-\text{COOH}$ , where  $x = 1, 3, \text{ or } 5$  (Fig. 2). However, if such components were present in one of the above reaction mixtures, then there is no reason to believe that they would be absent from the other. It is, therefore, suggested that since no components are common to the two reaction mixtures, esters of the form  $\text{HO}-x-\text{COOH}$ ,  $x = 1, 3, \text{ or } 5$  (Fig. 2) are not present in either reaction mixture.

The reaction mixture involving an excess of glycol is unlikely to yield products of the form  $\text{HOOC}-x-\text{COOH}$ ,  $x = 2, 4, \text{ or } 6$  (Fig. 2). However, if such compounds were found, they certainly should be present in the reaction mixture derived from the use of excess acid. Since we know that no components are common to the two reaction mixtures, it is believed that no compounds of the form  $\text{HOOC}-x-\text{COOH}$ ,  $x = 2, 4, \text{ or } 6$  (Fig. 2) are present in the reaction mixture made by using excess glycol.

From what has been said, it appears that the three components in the reaction mixture prepared using an excess of glycol are  $\text{HO}-x-\text{OH}$ ,  $x =$

6, 4, or 2 (Fig. 2). These are eluted at 20.5, 21.7, and 23.6 counts, respectively (Table XI).

When an excess of adipic acid is used, the arguments given previously can be applied. Thus, the components eluted at 21.2 and 22.6 counts (Table XII) are considered to be HOOC—4—COOH, and HOOC—2—COOH, respectively (Fig. 2).

1:4 Butanediol—adipic acid reaction mixtures all contain components analogous to those of the above 1:2 propanediol—adipic acid reaction mixtures. Further, from what has been previously stated, the analogous components will be eluted on the GPC at similar counts.

#### *GPC Analysis of Polyester Exudate*

Having suggested structures for the various components present in the polyester standards, an analysis of the exudates was undertaken.

Table XIII indicates the results of qualitative analysis, by gel permeation chromatography, of the two exudates. It is seen that the low molecular weight components of both exudates are eluted at the same times.

From the previous argument, it appears that the components of exudation at 26.4–26.5 counts and 28.7–28.8 counts arise from the stabilizer. The exudation component eluted at 24.7–24.8 counts is dodecanoic acid and/or a component of the stabilizer. The exudation component eluted at 23.5–23.6 counts is a component of the stabilizer and/or HO-1-T and/or

TABLE XIII  
Qualitative Analysis Results by GPC  
of the Exudates, and Standards

Counts at which eluted	Standard eluted	Amount and time at which components of the exudates were exuded	
		Drip exudate	Off-sheet exudate
28.8	—	—	minor
28.7	a major component of stabilizer	minor	—
26.5	a minor component of stabilizer	—	minor
26.4	—	minor	—
25.0	a major component of stabilizer	—	—
24.8	—	—	minor
24.7	—	minor	—
24.6	dodecanoic acid	—	—
23.6	HO—2—OH (Fig. 2)	minor	—
23.6–23.5	HO—1—T (Fig. 1)	—	—
23.5	a minor component of stabilizer	—	minor
21.8–21.7	T—2—T (Fig. 1)	—	—
21.7	HO—4—OH (Fig. 2)	major	major
20.5	HO—6—OH (Fig. 2)	—	—
20.4	—	—	major
20.3	—	major	—

HO—2—OH (Figs. 1 and 2). The component eluted at 21.7 counts is T—2—T and/or HO—4—OH (Figs. 1 and 2), and finally the component eluted at 20.3–20.4 counts is HO—6—OH (Fig. 2).

Exudation components eluted prior to 20 counts were of higher molecular weight species and detection of individual species was not possible with the columns used. One broad peak existed. The first discernible peak was that eluted at 20.3–20.4 counts.

The standards used to identify the components present in the exudation were not complete. There is a possibility that some of the products given in Figure 2 could have reacted with dodecanoic acid. No such molecules were synthesized in order to determine their elution count. It is, therefore, not known whether their elution would occur at a similar time as one or more components present in the exudation. However, it is felt that possible exuded components such as HO—1—T and T—2—T (Fig. 1), and those that might occur as a result of interaction between some compounds given in Figure 2 and dodecanoic acid, are not likely. This conclusion is reached because the lower molecular weight species present in the polyester possess the majority of the hydroxyl groups, thus indicating that the dodecanoic acid is mainly tied up with the higher molecular weight species and not with those low molecular weight species suggested as being components in the exudation.

It was previously mentioned that the exuded components eluted at 24.7–24.8 counts could be dodecanoic acid and/or a component of the stabilizer. Gas-liquid chromatographic analysis of both methylated exudations clearly indicated the presence of both these materials.

In summary, it is believed that the exudation components eluted in the GPC at greater than 20 counts are HO—6—OH, H—4—OH, H—2—OH (Fig. 2), components of the stabilizer, and dodecanoic acid.

The two samples of the exudation and the original polyester were analyzed by gel permeation chromatography using five Styragel columns in series of porosities  $10^6$ ,  $10^5$ ,  $10^3$ , 250, and 60 Ångströms. The chromatographs indicated that while both the exudates possessed similar molecular weight species, the off-sheet exudate was richer in the longer-chain-length molecules. This difference was reflected in the higher  $\bar{A}_w$  value of the off-sheet exudate (Table XIV).

TABLE XIV  
Molecular Weight Distribution of Exuded Samples

	$A_n$	$\bar{A}_w$	$\bar{A}_w/\bar{A}_n$	$\bar{M}_n$ by VPO
Original polyester	67.7	111	1.64	1430
Drip exudate	30.6	62.9	2.06	777
Off-sheet exudate	29.0	71.3	2.46	748

Comparison of the molecular weight distribution data of the exudates with the original polyester showed that while only 12% by wt of the original



TABLE XV  
Exudation Vs. Fractionation

	$\bar{A}_n$	$\bar{A}_w$	$\bar{A}_w/\bar{A}_n$	$\bar{M}_n$ by VPO	Acid value	Hy- droxyl value	Hy- droxyl conc.
Low molecular weight (fractionation 1)	40.2	67.0	1.67	804	2.3	49	0.70
Drip exudate	30.6	62.9	2.06	777	39.7	37	0.51
Off-sheet exudate	29.0	71.3	2.46	748	32.9	46	0.61

polyester was eluted at >20 counts, 33–34% by wt of the exudate was concentrated within that region.

Table XV compares the analysis of the exudates with the lowest molecular weight fraction derived from fractionation 1 of the original polyester. It is seen that, except for a great difference in acid value, the analyses are remarkably similar, the exudate possessing a slightly greater amount of low molecular weight material. Thus it is possible that the exudate is essentially the lowest molecular weight fraction isolated from the polyester by fractionation. Unfortunately, this fraction was not analyzed at that time by gel permeation chromatography with columns which would spotlight the lowest molecular weight components.

The question now arises as to the genesis of the exudate. It could be considered that it arises from a hydrolysis that is occurring on, or immediately beneath, the surface of the milled sheet. Alternatively, the exudate could consist merely of components of the unhydrolyzed plasticizer, etc.

One would expect that if the exudate were primarily hydrolyzed product, considerable difference would occur between its  $\bar{A}_w$ ,  $\bar{A}_n$ ,  $\bar{A}_w/\bar{A}_n$ , and  $\bar{M}_n$  values and those of the low molecular weight species resulting from the fractionation of the polyester. Table XV indicates that the difference is small. The exudate is considered to be essentially unhydrolyzed material exuding from the milled PVC sheets. However, a trace of hydrolysis could occur, accounting for the lower number-average chain lengths ( $\bar{A}_n$ ) of the exudate. The high acid value observed is puzzling. This cannot be explained by general hydrolysis since parallel increases in acid values and hydroxyl values would be expected.

## CONCLUSION

The results indicate that the exudation of certain polyester plasticizers from poly(vinyl chloride) contains a greater percentage of low molecular weight species than the original polyester. Further, such species are associated with a high hydroxyl group concentration. There is also clear evidence that the stabilizer used in the processing of the PVC is also a component of the exudation. It is interesting to note that there is no evidence of acid-terminated low molecular weight polyester molecules being present in the exudates. The only minor acidic component detected was dodecanoic acid.

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