# Studies in Estolides, Part III[1]: Plasticizer for Polyvinyl Chloride

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## ABSTRACT

Acetoxy butyl esters prepared from estolides (derived from castor oil fatty acids) were evaluated as plasticizers for poly (vinyl chloride) (PVC) resin. They showed limited compatibility. They were useful as secondary plasticizers for PVC along with dioctyl phthalate plasticizer. The properties of the plasticized stocks were generally comparable to the ones obtained by incorporating 12-acetoxy butyl oleate, the commercial secondary plasticizer. Among the estolides derivatives tried, the acetoxy butyl ester obtained from estolides of acid value 83 showed better performance.

## INTRODUCTION

Castor oil contains 90% hydroxy fatty acids. Hydrolysis of castor oil under high pressure (1) or Twitchell process conditions (2) directly yields estolides, a polymerized product with an average acid value (A.V.) of 50 and 85, respectively, and equally low hydroxyl content. Of late, polymeric plasticizers are finding acceptance. It is also well known that 12-acetoxy butyl oleate derived from castor oil is a secondary plasticizer for poly (vinyl chloride) (PVC). So it was of interest to study the usefulness of the acetoxy butyl esters of estolides, which have similar basic structure, as secondary plasticizers for PVC. In this paper these derivatives were evaluated and compared with 12-acetoxy butyl oleate as secondary plasticizers.

TABLE I

Characteristics of Materials[a]

| | A.V. | OH.V. | I.V. | S.V. |
|---|---|---|---|---|
| Castor oil fatty acids | 178 | 162 | 87 | 186 |
| 12-acetoxy butyl oleate | 0.9 | 0.6 | 74 | --- |
| Estolides (A.V. 83) | 83.4 | 68 | 89 | 194 |
| Acetoxy butyl esters from estolides A.V. 83 | 2.1. | 0.9 | 81 | --- |
| Estolides (A.V. 54) | 54 | 40 | 94 | 197 |
| Acetoxy butyl esters from estolides A.V. 54 | 1.24 | 5 | 79.2 | --- |

[a] Hydroxyl value, OH.V; Iodine value, I.V., Saponification value, S.V.

## EXPERIMENTAL PROCEDURES

Estolides of A.V. 83 and 54 were prepared according to the procedures of Kane (3). The estolides thus obtained were converted into acetoxy derivatives by refluxing with acetic anhydride in the presence of pyridine. The acetoxy estolides were isolated and subsequently esterified by refluxing with butanol in the presence of p-toluenesulfonic acid catalyst while removing the water of reaction as butanol-water azeotrope. The acetoxy butyl esters of estolides thus obtained were isolated and dried. The 12-acetoxy butyl oleate was prepared from castor oil by transesterification with dry butanol under reflux, using metallic sodium dissolved in butanol as catalyst. The product was isolated and acetylated as described earlier to obtain 12-acetoxy butyl oleate. The characteristics of these derivatives are given in Table I.

These derivatives were screened as plasticizers for PVC. Their performance was compared with that of dioctye phthalate (DOP). The compositions screened were made up of a mixture 100 parts of PVC and 50 parts plasticizer. The emprical screening test used consisted of gelling the resin mix for 5,10 and 15 min at 180 C in the form of a thin film over glass plates. The specimens were visually examined for clear and complete gelling and exudations. Compositions passing the test were futher milled, molded and subjected to physical testing. The screening procedure gave an indication of compatibility. As per this procedure, the acetoxy butyl esters were found to be useful as secondary plasticizers. Specimens were made from compositions that passed by mixing blends containing 10,20 or 30% of these esters in DOP, with PVC in the ratio 50:100 for 5 min and milling in a double roll steam heated mill for 10 min at 140 C.

The compositions that fused and gelled over the rolls and remained free from exudation were molded into 7 in. x 7 in. x 0.07874 in sheets under 300 lbs per sq. in. pres-

TABLE II

Physical Properties[a]

| Plasticizer blend contained acetoxy butyl ester from (P.h.r.) | (P.h.r.) | and DOP (P.h.r.) | 100% Modulus (Psi) | Tensile strength (Psi) | Elongation % | Shore hardness 10 Sec. cycle | Volablity % loss | Compatibility after days 30 | 60 |
|---|---|---|---|---|---|---|---|---|---|
| 1. NIL | 0 | 50 | 1041 | 2222 | 354 | 73 | --- | --- | --- |
| 2. Castor oil | 5 | 45 | 1077 | 2233 | 354 | 73.5 | 1.5 | G | G |
| 3. Estolides (AV 83) | 5 | 45 | 1101 | 2279 | 351 | 74.5 | 1.5 | G | G |
| 4. Estolides (AV 54) | 5 | 45 | 1075 | 2277 | 335 | 75.0 | 1.7 | G | G |
| 5. NIL | 0 | 45 | 1406 | 2376 | 325 | 77.0 | --- | --- | --- |
| 6. Castor oil | 10 | 40 | 1059 | 2243 | 359 | 77.5 | 1.7 | G | G |
| 7. Estolides (Av 83) | 10 | 40 | 1139 | 2304 | 340 | 78.0 | 1.7 | G | G |
| 8. Estolides (Av 54) | 10 | 40 | 1180 | 2334 | 324 | 78.5 | 1.7 | G | S |
| 9. NIL | 0 | 40 | 1707 | 2590 | 305 | 83 | --- | --- | --- |
| 10. Castor oil | 15 | 35 | 1129 | 2263 | 359 | 80 | 1.9 | G | G |
| 11. Estolides (AV 83) | 15 | 35 | 1186 | 2391 | 335 | 79.5 | --- | G | G |
| 12. Estolides (Av 54) | 15 | 35 | 1264 | 2378 | 314 | 80.5 | 1.7 | G | P |
| 13. NIL | 0 | 35 | 1871 | 2687 | 285 | 86 | --- | --- | --- |

[a] G, Good, S, Slight separation, P, Poor. phr., parts per hundred resin.

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[1] For parts I and II in the series, see Reference 3 and 4.

sure at 165 ± 2 C for 10 min. These sheets were conditioned at 23 ± 1 C for 7 days prior to physical testing. The tensile strength of the specimens were determined by ASTM methods. Measurements were made on a Zwick tensile tester and the elongation was measured at break. Hardness was determined using a Zwick durameter "A." Volatility loss was determined by heating 1 in dia specimens at 105 ± 1 C for 24 hr in an air oven. The specimens were stored at ambient temperature and visually examined for compatibility over a number of days. The evaulation data are presented in Table II along with those obtained for DOP alone as the sole plasticizer.

## RESULTS AND DISCUSSION

The data obtained show that increase in molecular magnitude of the estolides, (indicated by decreased A.V. of estolides.) decreased the plasticizer efficiency of the acetoxy butyl ester derivatives. Plasticizing efficiency of the acetoxy butyl esters as secondary plasticizers decreased in the order castor oil derivative, to estolides (A.V. 83), to estolides (A.V. 54). The properties of the compositions consisting of lower amounts of DOP alone are improved upon by the addition of these esters. However, the acetoxy butyl ester derivative obtained from estolides (A.V. 54) generally showed poorer performance, while the derivative obtained from estolides (A.V. 83) was comparable with 12-acetoxy butyl oleate within the experimental limits.

## ACKNOWLEDGMENTS

The study was supported by research grants from Indian Central Oil Seeds Committee. Advice received from late Prof. J.G. Kane.

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[Received May 31, 1978]