Polymerization of Unsaturated Fatty Acids*

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Introduction

The purpose of this paper is to describe a novel method for the preparation of polybasic fat acids by heat without a resulting appreciable loss in carboxy acidity. In this process decarboxylation and decomposition which heretofore invariably have accompanied heat polymerizations of fatty acids are prevented by the presence of moisture maintained in the reaction vessel by steam pressure. Besides its stabilizing effect on the carboxyl group, the moisture which is present also changes the composition of the polybasic fat acids in that the ratio of dibasic fat acids to higher polybasic fat acids is shifted considerably in favor of the dibasic acids as shown by polyamide preparations and molecular distillations. This process of polymerization in the presence of moisture has also been used to remove polyunsaturated acids from commercial oleic acid.

The results have been sufficiently promising to warrant the preparation of patent applications which are now pending with the expectation that the processes will find commercial utilization in the near future.

The subject of oil polymerization and the mechanism by which it takes place has been the basis for numerous investigations not only because of the widespread practical use of the process but also in order that a satisfactory working theory might be provided.

Most of the early work on this general subject dealt with the mechanism of oil polymerizations. Schreiber (1), who was one of the early workers in the field, advanced the theory that the isomerization of nonconjugated systems is a prerequisite to the polymerization reaction. Kappelmeier (2) suggested that the polymerization took place by a diene reaction or 1,4 addition of an isomerized molecule to a double bond of another molecule to form a substituted cyclohexene derivative. These theories were supported by Bradley and coworkers (3, 4) who investigated the course of polymerization of drying and semi-drying oils and determined the constitution of drying oil gels. During the course of the latter work, these investigators (5) isolated and characterized a fraction of polybasic acids which they termed "dimer" acids. According to the postulated mechanisms, the structural formula for dimerized linoleic acid would be,

\[
\text{CH}_\text{H}(_\text{CH}_\text{H}_2)_1\text{-CH-CH} = \text{CH}(_\text{CH}_\text{H}_2)\text{C-OH}
\]

\[
\text{CH}_\text{H}(_\text{CH}_\text{H}_2)\text{-CH} (\text{CH}_\text{H}_2)\text{C-OH}
\]

More recent work by Bradley and Johnston (3, 4) has shown that trimeric acids as well as dimeric esters are formed when methyl linoleate obtained from dehydroxylated castor oil is polymerized by heating. Cowan and coworkers (6) have shown by molecular distillations of materials obtained by the polymerization of methyl esters of linseed fatty acids that more than 50% of the polymerized esters are trimeric and higher polymeric in nature. When the polymerized esters are split, polybasic fat acids are formed. Polyamides of these materials have been suggested as adhesives and shellac substitutes, and the polyglycol esters of the polybasic fat acids were tested as rubber substitutes during the war. The proposed uses have encouraged various investigators to introduce methods for the preparation of these polybasic fat acids as such.

There are four principal methods for the preparation of polybasic fat acids. Unsatrated glycerides are polymerized by heat in an inert atmosphere until the gel point is nearly reached. This material is then split by alkali, and the acids are recovered by acidification of the soaps. Unpolymerized acids are removed by distillation under reduced pressure. In this process the yield of polybasic fat acids seems to be limited by the gel point of the oil used. The second process utilizes a methanalysis reaction of a drying oil and methanol in the preparation of the methyl esters of the unsaturated fatty acids. The methyl esters are then polymerized by heat, after which the material is distilled under reduced pressure to remove the unreacted portion. The residual esters are then split with alcoholic caustic solution, and the free acids are obtained by acidification of the soaps. These two methods are described in detail by Cowan (7, 8) and Bradley (9).

Percy and Ross (10) have described a method of preparing polybasic fat acids by the heat polymerization of the anhydrous sodium soaps of unsaturated fatty acids. The free acids are obtained by the acidulation of the soaps and are separated by distillation. Polybasic fat acids have been prepared by the heat polymerization of the fatty acids directly, with the separation being made by distillation. This would seem to be the most economical and direct method of preparing polybasic fat acids, but all of the reports on this procedure point out the fact that the fatty acids tend to decompose and decarboxylate when heated at or above 275°C, which is lower than the usual polymerization temperature of 300°C. In fact, it has been found in our laboratories that when linseed fatty acids are polymerized at 290 to 295°C, in an inert atmosphere, polybasic fat acids are obtained which constitute 50 to 55% of the weight of the starting acids but which have lost 30 to 35% of the original acidity by decarboxylation. Since it is desirable to prepare polybasic fat acids directly from fatty acids without an appreciable loss in carboxy acidity, the following procedure, which is the basis of this paper, was developed.

Experimental

The fatty acids used in the experimental work were commercial grade fatty acids. Heat polymerizations of the unsaturated fatty acids in the presence of moisture were carried out in a stainless steel pressure vessel which was heated by a direct gas flame.

Polybasic Fat Acids: A sample of the unsaturated fatty acids was put into the pressure vessel along with a small amount of water and heated to 330 to 360°C. The pressure was adjusted to the desired value of 85 to 400 lbs./in.² by the use of a vent valve. As an
alternate method, the pressure vessel was connected directly to a steam line. After the heating period of 3 to 8 hours the partially polymerized acids were dried, and the unreacted portion was removed by distillation under reduced pressure. The color of the polybasic acids in some runs was improved by bleaching with 3% of bleaching earth for 40 minutes at 80 to 90°C. The products were characterized by iodine values and neutralization equivalents. Results of typical polymerizations are tabulated:

**Polyamides From Polybasic Fat Acids:** Polybasic fat acids were used to prepare polyamides with both ethylene diamine and hexamethylene diamine. Polybasic fat acids were heated with stirring to 150°C, and with a slow stream of carbon dioxide gas being passed through them. A chemical equivalent of ethylene diamine (70% aqueous solution) was added slowly through a tube leading to the bottom of the reaction vessel. When all of the ethylene diamine had been added, the temperature was raised gradually to 200°C, and the pressure was lowered to 10 mm. of Hg. After one hour at these conditions a sample was removed and titrated with both acid and base to determine which ingredient was in excess. A calculated amount of the lesser ingredient was added, and the temperature was raised to 250 to 260°C. under 10 mm. of Hg. pressure. Polyamides having molecular weights of 6,000 to 10,000 were obtained in this manner.

Chemical equivalents of polybasic fat acids and hexamethylene diamine were heated in the presence of carbon dioxide gas at 150°C. for one hour. The temperature was then raised to 200°C, and the pressure was reduced to 10 mm. of Hg. After one hour, a sample was removed and titrated with acid and base to determine the ratio of free carboxyl to free amino groups. Any inequalities were adjusted, and the resin was heated to 250 to 260°C. under a pressure of 10 mm. of Hg. Polyamides having molecular weights of 28,000 to 29,000 were obtained by this method.

**Molecular Distillations:** The methyl esters of polybasic fat acids from various raw materials were prepared. They had free fatty acid values of about 2% as oleic acid. The esters were heated to 300°C. under 4 mm. of Hg. pressure to remove gases and any unreacted monomeric esters. Samples were weighed into a Hickman molecular still and were distilled at temperatures up to 250°C. under a pressure of one to two microns. The distilled esters were mobile liquids having free fatty acid values in the order of 0.2% as oleic acid.

**Removal of Polyunsaturated Acids From Commercial Oleic Acid:** Only slight variations in the polymerization process need be made for removing polyunsaturated acids from commercial oleic acid. Usually a shorter time and a lower temperature are used.

Commercial oleic acid was heated in an autoclave for three hours at 330 to 340°C. under a steam pressure of 300 lbs./in.². Monomer acids were removed from the polymerized acids by distillation under reduced pressure. Spectrophotometric results showed that the polyunsaturated acid content had been substantially lowered. Results of a typical run are tabulated.

**Discussion**

The process for the preparation of polybasic fat acids directly from the acids is a very simple one involving two steps which are polymerization and separation. It is based on the discovery that small amounts of water maintained in the reaction vessel almost completely stop decomposition of the fatty acids at polymerization temperatures. The use of moisture in conjunction with heat and moderate pressures is a very simple process to apply commercially, and perhaps because of its simplicity is surprisingly effective. The various factors effecting this process are the nature of the raw material used, polymerizing temperatures, time of polymerization, moisture present, and catalysts.

**Raw materials:** Fatty acids from any of the many drying or semi-drying oils may be used, but from a standpoint of economics, fatty acids recommended are those from soy, cottonseed, corn, and linseed oils. In this process the yield of polybasic fat acids obtained seems to be limited by the amount of polyunsaturated acids present in the raw material used (Table I). In general, the color and quality of polybasic fat acids are dependent on the color and quality of the raw material. The amount of polyunsaturated fatty acids having more than two double bonds to a molecule is a factor in determining the amount of tribasic and higher polybasic fat acids formed during the polymerization. This is demonstrated by the fact that linseed fatty acids, which contain considerable linolenic acid, produce more tribasic acids than do fatty acids from soy oil which have much lower linolenic acid content.

**TABLE I**

<table>
<thead>
<tr>
<th>Raw Material</th>
<th>I.V.</th>
<th>Yield of Polya inherent Fatty Acids</th>
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</thead>
<tbody>
<tr>
<td>Soy Acids</td>
<td>137</td>
<td>58.8</td>
</tr>
<tr>
<td>Linseed Acids</td>
<td>190</td>
<td>64.2</td>
</tr>
<tr>
<td>Cottonseed Acids</td>
<td>209</td>
<td>68.8</td>
</tr>
<tr>
<td>Cottonseed Fats Acids</td>
<td>134</td>
<td>50.5</td>
</tr>
<tr>
<td></td>
<td>109</td>
<td>39.5</td>
</tr>
</tbody>
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**Time and Temperature of Polymerization:** The polymerizing temperatures used were from 275 to 370°C. The temperature at which the reaction is carried out does not seem to be critical, but there is an interrelationship between time and temperature in that higher temperatures shorten the time of polymerization appreciably. For example, about the same degree of polymerization is attained in six to seven hours at 350°C., as results from an 18-hour heating period at 290°C. In order to obtain a high degree of polymerization in a reasonable length of time, temperatures of 330 to 360°C. are recommended. At these temperatures, polymerization is virtually complete in three to eight hours.

**Presence of Moisture:** The presence of moisture in the polymerization reaction produces remarkable