This process relates to an improved method for making heptaldehyde and undecylenic acid from castor oil by destructive distillation.

According to previous processes, castor oil or an ester of ricinoleic acid is heated with or without catalysts, preferably under reduced pressure, at temperatures around 400° C. and the distillate therefrom fractionated. The yield of heptaldehyde is usually small and its cost high if castor oil is employed, as about 50 to 75 percent of the oil goes over into an infusible, insoluble, spongy mass having no practical value. It is removed only with difficulty from the stills and represents an economic loss.

The object of the present invention is to prepare heptaldehyde and undecylenic acid from castor oil in good yield without the formation of the above mentioned insoluble spongy mass; and to accomplish this in a manner more economical and more adapted for large scale manufacture than previous processes.

We have discovered that heptaldehyde and undecylenic acid may be obtained in good yield by destructively distilling in vacuo a mixture of castor oil and an acidic resin such as colophony, gum dammar, kauri, Congo, copals, ester gums and the like, without formation of infusible, insoluble, spongy still residues. The still residues obtained according to our process are fluid while hot and are readily run out from the still. They constitute a useful by-product from the operation, thus cutting down the overhead costs of the heptaldehyde.

We are aware that in the past, castor oil has been heated with various resins to obtain fluid compositions which are either simple solutions of the resin in the oil or ester-like combinations of the acidic resin and the oil. Such processes have been carried out at relatively low temperatures so that no appreciable cracking of the castor oil to form heptaldehyde occurs. The essential features of our process are that the heating of the castor oil and resin is carried out at temperatures in excess of the decomposition point of the castor oil so as to form heptaldehyde and undecylenic acid which may be condensed, and at the same time to prevent formation of an insoluble, worthless still residue by taking up the still residue as fast as it forms in a suitable gum or resin so that it may be run out.

For practicing this invention the following examples are given. The parts given are by weight.

**Example 1**

Raw castor oil (2 parts) is mixed with 1 part of wood rosin in a capacious still fitted with an inlet capillary tube for aspirating air or an inert gas such as nitrogen or carbon dioxide through the mass. The still is connected to a downward condenser attached to a water-cooled receiver which is in turn connected to a vacuum pump. The still is heated to about 400–450° C. so that the temperature of the contents is 300–340° C. and the distillation is carried out under a pressure of from 30 to 60 m.m. of mercury until no further distillate comes over in the receiver. During this process air, nitrogen, or carbon dioxide is continuously bubbled through the hot mass in the still. The distillate obtained contains rosin, rosin oil, heptaldehyde, water, and undecylenic acid together with polymers of undecylenic acid. The heptaldehyde and undecylenic acid may then be recovered from this distillate by suitable fractionation in the usual way. The still residue due to its fluid nature is readily run out while hot and the still charged for the next run. The still residue forms a solid rubber-like mass readily soluble in benzene and having potential commercial value.

The proportion of rosin to castor oil may be varied within wide limits. The temperature of the mixture should, however, in all cases exceed 290° C., as practically no heptaldehyde is formed below this cracking temperature. The optimum temperature range is 310–340° C.

**Example 2**

Instead of rosin, an equal weight of ester gum (acid No. 8) (abietic glyceride) may be used in the procedure described above at a
temperature of 330–340° C. Heptaldehyde and undecylenic acid are obtained together with a fluid still residue which is not as rubbery as that obtained in Example 1.

Example 3

Castor oil is mixed with 25 percent of its weight of kauri gum and subjected to destructive distillation at 340° C. under 50 m.m. pressure as described in Example 1, to obtain heptaldehyde and undecylenic acid.

Instead of the above resins one may use other acidic gums, both natural and synthetic, such as dammar, Congo, and the various copals or the condensation products thereof with phenols and aldehydes.

Furthermore mixtures of any two or more of the above acidic gums or resins may be employed in the condensation with castor oil, and pressures higher or lower than that indicated may be employed during the destructive distillation. Additional catalysts for accelerating the decomposition may also be added in small amounts up to 2% by weight on the oil. These include acidic and basic substances such as lime magnesia, zinc oxide, boric oxide and phosphoric acid.

What we claim is:

1. A process for making heptaldehyde and undecylenic acid which comprises vacuum destructively distilling a mixture of raw castor oil and ester gum under vacuum at a temperature of 300–340° C. and condensing the vapors.

2. A process for making heptaldehyde and undecylenic acid which comprises vacuum destructively distilling a mixture of raw castor oil and an acidic resin to inhibit the condensation of the castor oil to an insoluble mass, at a temperature above the decomposition point of the castor oil, and condensing the vapors.

3. A process as set forth in claim 2 in which one of the group consisting of air and inert gases is aspirated through the mixture during the distillation.

4. As a new composition of matter the still residue by-product resulting from the manufacture of heptaldehyde and undecylenic acid as set forth in claim 2, said material being a benzene-soluble plastic mass.

5. The process for making heptaldehyde and undecylenic acid which comprises vacuum destructively distilling a mixture of raw castor oil and a member of the group consisting of colophony, ester gum, dammar, kauri, Congo, copals, and mixtures thereof, at a temperature above the decomposition point of castor oil, and condensing the vapors.

6. The process for making heptaldehyde and undecylenic acid which comprises destructively distilling raw castor oil with one half its weight of resin under vacuum at a temperature of 300–340° C. and condensing the vapors.

7. The process for making heptaldehyde and undecylenic acid which comprises de-

What we claim is:

8. The process for making heptaldehyde and undecylenic acid which comprises destructively distilling castor oil with resin under vacuum at a temperature above the decomposition point of castor oil and condensing the vapors.

9. A process as described in claim 8 in which ester gum is used in place of resin.

10. The process for making heptaldehyde and undecylenic acid which comprises destructively distilling castor oil with a synthetic acidic resin under vacuum at a temperature above the decomposition point of castor oil and condensing the vapors.

In testimony whereof we affix our signatures.

HERMAN A. BRUSON.

JACK D. ROBINSON.