SEPARATION OF GAMMA-VALEROLACTONE FROM WATER

George E. Ham, Dayton, Ohio, assignor to Monsanto Chemical Company, St. Louis, Mo., a corporation of Delaware

Application March 25, 1948, Serial No. 17,696

3 Claims. (Cl. 360—344)

This invention relates to a method of separating lactones from water solutions, particularly water solutions containing relatively small proportions of the lactone. More particularly the invention relates to methods of extracting lactones from completely miscible mixtures of lactones and water.

In the preparation of synthetic fibers from polymers of acrylonitrile, particularly those of 70 percent or more by weight of acrylonitrile and up to 30 percent of other polymerizable monomers, it is customary to dissolve the polymer in a suitable solvent and to extrude the solution so prepared through an orifice, or a spinnerette comprising a plurality of orifices, into a medium which removes the solvent and coagulates the polymer as a continuous solid fiber. The said medium must be a liquid which dissolves the polymer solvent but which is a nonsolvent for the polymer. Many of the acrylonitrile polymer solvents are water soluble and when these are used the fibers may be extruded into water or an aqueous medium.

In application, Serial No. 351, filed January 2, 1948, by Carroll A. Hochwalt, now abandoned, there are described and claimed methods of preparing a synthetic fiber from solutions of polyacrylonitrile and acrylonitrile copolymers in butyrolactone by the aforesaid conventional spinning technique. When the butyrolactone solutions are extruded into water the butyrolactone is dissolved by the water and accumulates in the aqueous bath, from which it must be recovered to effect an economically practicable fiber production method. Similarly when gamma-valerolactone is used as a solvent for copolymers of acrylonitrile, methacrylonitrile and vinyl acetate, which method is described and claimed in application, Serial No. 17,111, filed March 25, 1948 by Carroll A. Hochwalt, now abandoned the gamma-valerolactone must be recovered from the aqueous bath for reuse.

Although the spinning of acrylonitrile polymers and copolymers from solutions in butyrolactone or gamma-valerolactone may be effectively accomplished using water as the spinning medium, it is usually more effective to spin the polymer solutions into a medium which reacts chemically with the lactones and thereby more effectively removes solvent from extruded fiber. Methods of this type are described and claimed in copending application, Serial No. 17,112, filed March 25, 1948, by Carroll A. Hochwalt, in which method an aqueous alkaline bath is used which converts the lactones into water soluble salts of the corresponding hydroxy acids. The spent spin-bath solutions containing substantial proportions of the dissolved salts of the hydroxy acids must be processed to recover the lactones. This is accomplished by acidifying the bath with any inexpensive acid, such as sulfuric and hydrochloric acid to obtain an aqueous solution of the regenerated lactone.

The purpose of the present invention is to provide a method of separating the gamma-valerolactone, butyrolactone, or any other stable lactones having five or six member lactone rings, from the high concentrations of water as occur in the waste water from wet spinning operations. A further purpose of the invention is to provide a continuous cyclic process of spinning acrylonitrile fibers from lactone solutions with the effective recovery and reuse of the solvent.

It has been found that stable lactones having the structure:

wherein R is a divalent aliphatic hydrocarbon radical of the group consisting of radicals having three or four carbon atoms between the carbonyl and oxygen radicals, such as gamma-valerolactone and butyrolactone, may be conveniently separated from dilute water solutions by extraction with an aromatic hydrocarbon. Suitable hydrocarbons are benzene, toluene and the various isomeric xylenes, of these benzene being the most efficient and least expensive, is more economically feasible. The aqueous wastes from wet spinning operations involving the use of lactones as solvents will usually contain from 5 to 25 percent by weight of the lactone, the balance being essentially water. After a quantity of the aqueous liquor is mixed with a small proportion of an aromatic hydrocarbon, for example from 5 to 25 percent by weight, the mixture will separate into two distinct liquid phases, of which the upper phase will be the hydrocarbon containing a high proportion of the lactone. The lower aqueous phase, which contains a much smaller proportion of the lactone, may again be treated with a further quantity of the hydrocarbon and another substantial separation of the lactone thereby effected. Obviously as many extractions may be used as desired to effect an economical operation. Continuous countercurrent extracting methods are also adaptable in apparatus conventionally used to effect liquid extractions.

Further details of the method of practicing
this invention are described with reference to the accompanying drawings of which:

Figure 1, is a ternary diagram showing the phase relationship and mutual solubilities of water, benzene, and gamma-valerolactone.

Figure 2, is a ternary diagram showing the phase relationship and mutual solubilities of water, toluene and gamma-valerolactone.

The diagram of Figure 1, demonstrates graphically that mixtures of large proportions of gamma-valerolactone and small proportions of both water and benzene are entirely miscible. That is, with respect to proportions represented by the area above and to the right of the curved line DE, only a single liquid phase is present. Although water lactone mixtures and benzene lactone mixtures are miscible in all proportions, all three component mixtures represented by the diagram area to the left and below line DE will contain two liquid phases. The diagram also shows a series of diagonal lines, FC, FD, KE, and LN, which are known as "tie lines," the axial intercepts of which represent the distribution of the lactone in the aqueous and hydrocarbon phases. For any mixture of water, gamma-valerolactone and benzene there is a tie line which passes through the point on the diagram representing that composition and has a slope such that the intersections of the line with the base lines of the diagram show the composition of each phase. Compositions which fall between the tie lines, as of Figure 1, may be determined by interpolation or reasonable extrapolation. It will be readily apparent from the ternary diagram that the hydrocarbon layers will contain very high proportions of the gamma-valerolactone from which the pure lactone can be separated by evaporation of the hydrocarbon. Because the hydrocarbons and the lactones form normal distillable mixtures free from azetropes, a rapid and effective separation of the hydrocarbon from the lactone is possible.

Figure 2, shows the ternary system which is involved in the use of toluene as the extractant in place of the benzene. It will be apparent that the gamma-valerolactone may be effectively separated from water by the use of toluene, although the distribution ratio of the gamma-valerolactone in water and toluene is not quite as favorable as in the case of benzene.

Further details of the practice of this invention are set forth with respect to the following example.

Example

An aqueous solution of 20 percent by weight of gamma-valerolactone was mixed with one-fifth its weight of benzene. After the two phase system reached a state of equilibrium, the two phases were separated. The benzene layer was fractionated in a distillation column using a 5:1 reflux ratio at atmospheric pressure and virtually complete separation of benzene and gamma-valerolactone was effected. The benzene layer was found to contain 29.7 percent by weight of gamma-valerolactone which was 92.2 percent of the gamma-valerolactone in the aqueous solution. Thus a single extraction with benzene reduced the gamma-valerolactone content of the aqueous solution from 20 percent to 8.5 percent. The gamma-valerolactone recovered was of sufficient purity (N=1.4923) to dissolve a copolymer of 84 percent acrylonitrile, 11 percent methacrylonitrile, and 5 percent vinyl acetate. A temperature of 100°C. was used to effect the solution but the resulting solution was stable at room temperature.

When countercurrent extraction apparatus is used substantially complete separation of the lactone from water is possible thereby avoiding the costly evaporation of water. Because of the much higher concentrations of the lactone in the hydrocarbon solutions the evaporation of a much smaller proportion of the hydrocarbon is relatively less costly.

Although the invention has been described with respect to a specific example showing a single stage extraction, it should be apparent that multiple stage extractions, and especially extractions utilizing countercurrent flow are readily practicable. The scope of the invention is not limited to the extent that the details are incorporated in the following claims.

I claim:

1. A method of separating gamma-valerolactone from aqueous solutions thereof which comprises mixing benzene with the said aqueous solution, in sufficient amount to produce two liquid phases, separating the two liquid phases so produced, evaporating the benzene from the non-aqueous phase, and recovering the separated gamma-valerolactone.

2. A method of separating gamma-valerolactone from aqueous solutions thereof which comprises mixing toluene with the said aqueous solution, in sufficient amount to produce two liquid phases, separating the two liquid phases so produced, evaporating the toluene from the non-aqueous phase, and recovering the separated gamma-valerolactone.

3. A method of separating gamma valerolactone from aqueous solutions thereof, which comprises mixing the aqueous solution with a hydrocarbon of the group consisting of benzene, toluene and the xylenes, in sufficient amount to produce two liquid phases, separating the two liquid phases so produced and evaporating the hydrocarbon from the non-aqueous phase.

GEORGE E. HAM.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

<table>
<thead>
<tr>
<th>Number</th>
<th>Name</th>
<th>Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,388,979</td>
<td>Isham et al.</td>
<td>Sept. 26, 1944</td>
</tr>
<tr>
<td>2,432,447</td>
<td>Scheiderbauer</td>
<td>Dec. 9, 1947</td>
</tr>
</tbody>
</table>

FOREIGN PATENTS

<table>
<thead>
<tr>
<th>Number</th>
<th>Country</th>
<th>Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>883,764</td>
<td>France</td>
<td>Mar. 29, 1943</td>
</tr>
</tbody>
</table>