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METHOD FOR MANUFACTURING POLYMERIZED FATTY ACIDS

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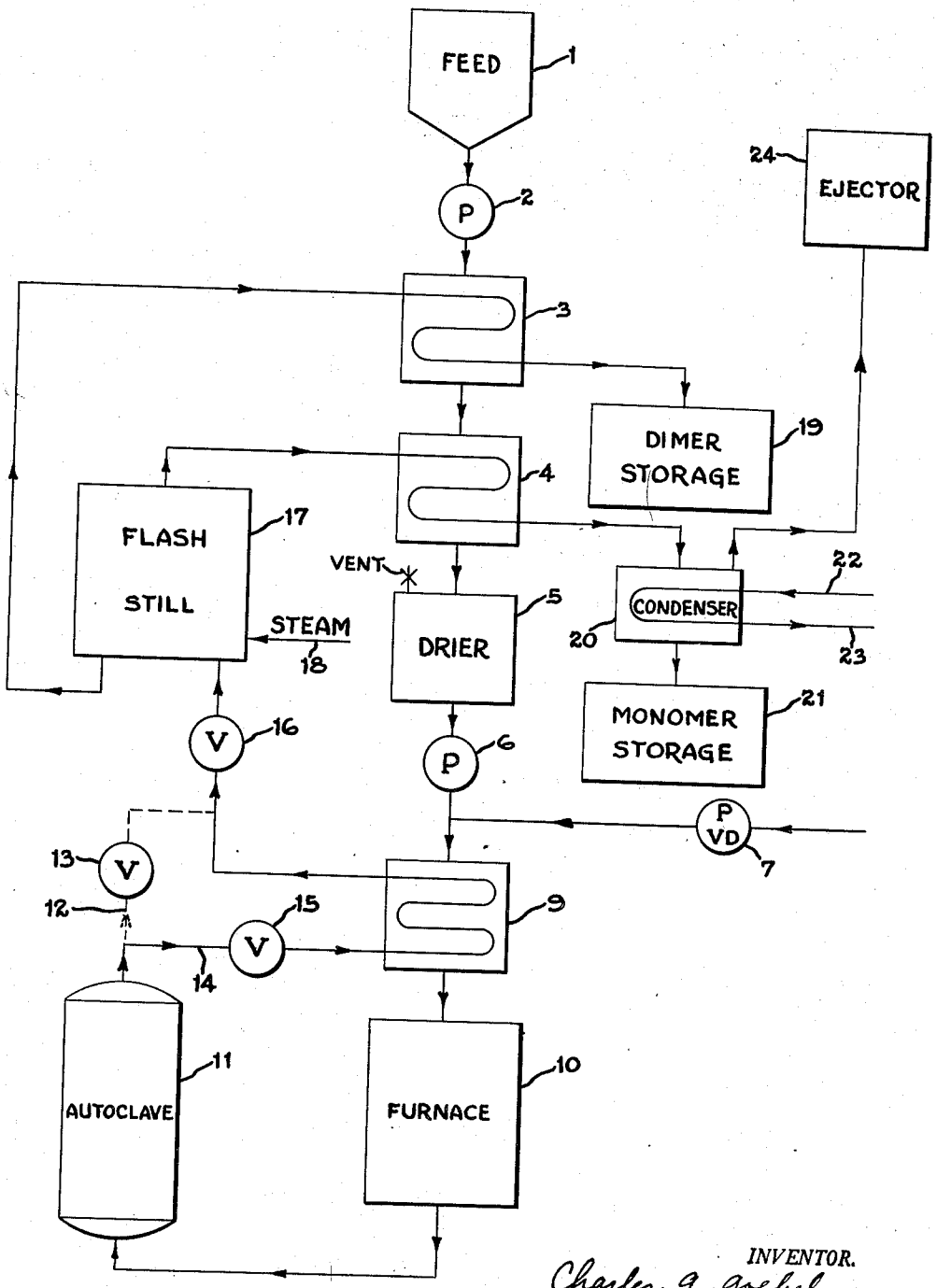

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METHOD FOR MANUFACTURING POLYMERIZED FATTY ACIDS

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This invention relates to a method for effecting the continuous polymerization of the polyunsaturated components of a mixture of fatty acids, and to their separation from the monounsaturated and saturated components thereof. The general method of accomplishing this result involves the dimerization of the polyunsaturated components thereby increasing their boiling points, which facilitates subsequent separation of the respective components, as by distillation. The inventions disclosed and claimed in my copending applications Ser. Nos. 678,160 and 681,765, now issued as Patent No. 2,482,760 and Patent No. 2,482,761 respectively, provide methods by which dimerization is conducted without the substantial losses and deterioration of the products which normally result from the high temperature requisite to accomplish the dimerization. More specifically, application Ser. No. 678,160 discloses a method of manufacturing pure oleic acid from commercial red oil by dimerizing the polyunsaturated components of the red oil and then separating them from the monounsaturated components. Application Ser. No. 681,765 discloses a method of manufacturing dimers by polymerizing the polyunsaturated components of fatty acids, such as linseed oil or soybean oil fatty acids, from which saturated and monounsaturated acids may then be removed if necessary or desirable. The present application is a continuation-in-part of each of these earlier applications.

Each of these methods is characterized by the utilization of a relatively small amount of water maintained in solution in the fatty acids by application of pressure during a polymerization heat treatment of intensity which would otherwise be destructive to the carboxyl radicals of the fatty acids.

The chief problem in utilizing the methods of either of these inventions is to carry them out on a commercial scale without concomitant equipment of prodigious proportions and cost. The heating of large bodies of fatty acids to high temperatures with the use of quantities of water which establish corresponding high pressures, and the holding of the acids at such temperatures and pressures over prolonged periods of time, pose a problem of providing practical equipment which will be of reasonable proportions as to size and cost in relation to throughput.

Expensive corrosion resistant alloys are required for the fabrication of pressure vessels which permit the employment of temperatures and pressures of the order involved without ruinous corrosion and forbidding safety hazards. But

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vessels fabricated from such alloys of a size adequate to provide throughput which can be characterized in tons per day, rather than pounds per day, are enormously expensive, particularly if their utilization is limited to batch processing as distinguished from continuous processing.

It is the object of this invention to provide apparatus for continuously polymerizing the polyunsaturated components of a mixture of fatty acids and separating them as dimer acids from the less unsaturated components without prohibitive equipment costs. It is also the objective to provide a practical commercial process for effecting this dimerization and separation which permits a throughput which is high in relation to the amount of equipment and to the cost of equipment utilized in the operation.

This invention involves establishing a continuous flow of a stream of mixed fatty acids from a stock storage tank to individual storage tanks in which the separated components are received at the end of the process. The apparatus comprises means for pumping under the pressure requisite at each stage of the operation and means for heating and cooling the stream at predetermined points in the cycle.

The fatty acids which are adapted to be used as raw materials, or starting materials, in this process are mixed fatty acids which contain polyunsaturated components and less unsaturated components such as the fatty acids of linseed, soybean, cottonseed, corn and fish oils. The fatty acids of all of these oils provide substantial yields of polymerized acids. On the other hand, red oil (commercial oleic acid) or the fatty acids of tallow, lard oil or the like may be processed, although in such case, the primary purpose would probably be the enhancement of the value of the fatty acids themselves, rather than the production of the polymerized acids which would be recovered as by-products. For convenience in describing this invention, all of the fatty acids which contain polyunsaturated components and less unsaturated components will be termed the fatty acids of drying and semi-drying oils to distinguish them from fatty acids such as commercial stearic which is substantially devoid of polyunsaturants.

The stream of mixed fatty acids is first conditioned for polymerization by the introduction of substantially 1–5% water by weight. It is the function of the water which is injected into the fatty acids to protect them against deterioration or decarboxylation which they otherwise would suffer under the temperatures employed in the operation. The amount of water, percent-

agewise, is not precisely critical and, of course, will vary in accordance with the permissible pressures for which the equipment is designed, the greater the percentage of water the greater the resultant pressure and vice versa. The apparatus components of the system, including the pumps, are adapted to operate at pressures which, at polymerizing temperatures, will prevent vaporization of the water, so that the water remains in the fatty acids and affords its full protective effect.

Quantities of water substantially greater than 5% have not been found to be desirable since they do not confer additional protective benefits and they do increase the operating pressures which are required to hold them in liquid condition or in solution in the fatty acids. On the other hand, substantially less than 1% by weight of water based on the weight of the fatty acids may be insufficient to accomplish the desired inhibitory result. Best operation is obtained by selecting a percentage of water within approximately the range indicated and then adjusting the water content of the fatty acids being treated to maintain the water content selected.

Preferably the fatty acids are dried under vacuum to such degree that their moisture content is of no significance from the point of view of the generation of steam pressure within the system, and then the predetermined amount of water is added. The maintenance of the predetermined content of water in the flowing stream insures the required stability of operational conditions and the continuation of the chosen relationships of temperature, pressure and duration of treatment for each quota of the stream. If the stream of fatty acids were not first dehydrated it might vary in moisture content and this would unbalance the operating conditions. Moisture contents above the expected might even endanger the equipment itself as a result of development of excessive pressure.

The watered stream of fatty acids is next heated under pressure to effect polymerization after which the pressure is released to flash distill the monomers from the polymers. Considerations pertinent to the relationship of the preferred method and the most economical apparatus are several and interrelated. Although polymerization commences slowly somewhere in the neighborhood of 250° C., with most fatty acids, the rate of polymerization substantially doubles with each 10 to 15° C. temperature rise. It follows that at substantially 400° C. the time required for polymerization is but a fraction of that necessary at 250° C. Thus the size of the equipment required to hold the body of fatty acids being polymerized for the time requisite decreases in inverse ratio to the temperature utilized.

Since equipment suitable for holding the hot corrosive acids under high pressure must necessarily be stainless steel or the equivalent, and relatively thick walled, it is desirable to minimize its size and hence its overall cost in order to reduce the fixed cost component of each unit of throughput. But, on the other hand, it is futile to attempt to reduce the fixed cost component by the use of high temperatures if the saving is nullified by the added operating cost inherently involved in the utilization of the higher temperatures.

I solve this problem by heating the stream of fatty acids to a polymerizing temperature above that which is requisite later to flash distill the stream, but chill it after polymerization to distillation temperature by heat exchange with the infeed, whereby the high temperature and concomitant economical equipment are had at no operating cost greater than that represented by the radiation losses, which may be minimized by appropriate utilization of insulation.

Instead of utilizing the heat not required for distillation to preheat the infeed, it may be utilized to generate the steam required for other steps of the process, such as stripping steam or the operation of vacuum ejectors or even the high temperature steam for a countercurrent fatty acid splitting tower. By this device, the stream of fatty acids is polymerized at optimum temperature and flash distilled at a lower, but also optimum, temperature. By this method, I avoid flash distillation temperatures which might tend to distill over the polymer with the monomer or which might tend to be destructive to the acid radicals after the release of pressure, which permits the moisture content to volatilize.

While processing of the stock through the polymerizer and flash still preferably proceed as sequential steps to which the continuous stream of stock is subjected, the polymerized component may also be recycled through the polymerizer, if desired, whereby the material passing through the polymerizing zone more than once becomes more highly polymerized than would otherwise be the case.

The apparatus of this invention is illustrated diagrammatically in the accompanying flow sheet according to which the material to be processed is drawn from feed tank 1 by pump 2 which forces it through heat exchangers 3 and 4 and drier 5. In heat exchanger 3, heat is withdrawn from the dimerized acids which constitute the still residue, and in heat exchanger 4, heat is withdrawn from the monomer acid vapors resulting from distillation. Drier 5 is utilized for the purpose of insuring a standard moisture content for the stream of material to be treated.

The material is fed from drier 5 to pump 6 which forces it under high pressure through the apparatus in which the polymerization is accomplished. A pump 7, preferably a metering pump, forces a small but measured stream of water into the material discharged from pump 6 to provide a water content of substantially 1 to 5%. After this the material enters heat exchanger 9 in which it withdraws heat from the material which has been polymerized, but has not yet been distilled.

The material being processed then passes from the heat exchanger through a furnace 10 in which it is heated to a temperature approximating but not equalling, the maximum temperature to be utilized in the process. From furnace 10 the fatty acids pass into autoclave 11 which is provided with baffles (not shown) which maintain the stream like character of the flow. The dimerization is completed in the autoclave and, since this is an exothermic reaction, the temperature of the fatty acids tends to rise above the temperature to which they were elevated in furnace 10. From autoclave 11 the fatty acids may be conducted by line 14 back to heat exchanger 9 where they are cooled by the incoming feed directed to furnace 10. Preferably the amount of heat removed is sufficient to reduce the temperature of the fatty acids to just that amount necessary for subsequent flash distillation. In order to control the temperature of the fatty acids to be subjected to the flash distilla-

tion, heat transfer device 9 may be bypassed by line 12, so that the amount of fatty acids subjected to the cooling action can be proportioned, in relation to the fatty acids fed directly to the flash still, by control valves 13 and 15. This arrangement provides flexibility adapting the equipment for the utilization of various fatty acid stocks and various polymerization temperatures.

From autoclave 11 and exchanger 9, the fatty acids are delivered through pressure control valve 16 which maintains pressure in the system between it and pump 6. This pressure must at all times be sufficient to hold the moisture present in solution or in the liquid state (whichever it is) to protect the carboxylic radicals of the fatty acid from the decomposition which the high temperature tends to induce.

After passing through pressure control valve 16, the fatty acids are fed into flash still 17. The monomer acids, that is, the unpolymerized fatty acids, volatilize or vaporize rapidly, i. e., they flash. In other words, they vaporize to be ultimately recovered as condensate and the higher boiling point polymer or dimer acids are withdrawn as still residue. The flash still 17 is operated under a vacuum and steam is introduced into its lower portion by means of line 18 to strip unpolymerized fatty acids from the still residue. This residue is withdrawn from the bottom of the still and conducted to heat exchange device 3 where it is cooled by the fatty acid infeed, after which it is conducted to storage container 19.

The distillate is conducted from the flash still 17 to the heat exchanger 4 where it supplies heat to the incoming feed of fatty acids. The distillate then passes to condenser 20 from which it is delivered to storage tank 21. The condenser is provided with cooling water by lines 22 and 23 which are utilized to maintain the condenser at the desired operating temperature. An ejector or evacuator 24 is connected with condenser 20 and is utilized to draw a vacuum on the condenser and the flash still. In accordance with accepted distillation practices, it is desirable to maintain as great a vacuum as possible in the flash still within the limits of economical size of the evacuator or eductor. Under less favorable vacuum conditions it may be necessary to increase the temperature of the stock in the flash still in order to effect volatilization of some of the less volatile monomeric materials, but, in this respect, it should be remembered that the protective water is no longer present in the stock and it is desirable therefore to hold the temperature as low as possible in order to avoid deterioration or decarboxylation of the products during distillation.

The exact temperature and time conditions employed for effecting the polymerization may be governed by the nature of the infeed stock, and of course, the specifications of the equipment which is available. In general the time during which the fatty acids are subjected to the polymerizing temperature will be governed by the nature of the fatty acid stock and the degree of polymerization which is desired, as well as by the actual polymerizing temperature. Thus, the polymerizing operation may be completed to the extent desired in as little as approximately 20 minutes, or the processing may be continued for as long as two hours or more. Since the polymerization is conducted in a baffled autoclave or elongated conduit, the time for polymerization may be controlled conveniently by adjustment of the rate of flow of material through the system.

By way of illustration, but not by way of limitation, polymerization may proceed, for example, at a temperature of approximately 385° C. under a pressure of 600 lbs. per square inch for a period of from 20 to 60 minutes. There is also considerable latitude in the exact conditions under which flash distillation is conducted. For example, with a polymerizing temperature of 350° to 400° C., the dimer-monomer mixture may be cooled to within the range of 260° to 360° C. before flash distilling. Preferably, but not necessarily, flash distillation may occur under an absolute pressure of substantially 10 millimeters of mercury, and monomer vapors are stripped later from the residue by introducing saturated steam at approximately 115° C., in the proportion of substantially 1 lb. of steam to each 10 to 20 lbs. of residue.

While polymerization temperatures in excess of 400° C. have not been mentioned specifically, it is to be understood that temperatures up to those destructive to the fatty acids themselves may be employed provided the water content of the fatty acids is increased proportionately to provide proper protection against decarboxylation. However, 375° to 400° C. would appear to constitute the operational range which is optimum at present in view of the limitations of presently available materials.

Obviously, precise operating conditions must be determined in relation to the nature of the fatty acid stock being treated and the end products desired. For instance, the temperature proper for flash distillation necessarily varies with the ratio of monomer to polymer after completion of polymerization. The greater the proportion of monomer the greater must be the total available heat necessary to distill it.

The disclosure has been made primarily in relation to the processing of fatty acids such as those obtained from soybean or cottonseed oil, i. e., acids in which the prevailing chain length is 18 carbon atoms. For acids of greater chain length distillation temperatures should be properly adjusted. Likewise, if the process be practiced to remove very small percentages of polyunsaturants from the acids so that the monomers are present in predominant proportions, then each distillation temperature must be individually calculated. Since polymerization is an exothermic reaction, the increase in temperature due to it must be taken into account in all calculations.

While it might be desirable in some cases to conform the specifications of a given polymerization plant to the requirements of the processing of a specific fatty acid stock, the apparatus of this invention has the virtue of flexibility, that is, a single piece of equipment may be used to process many types of raw material by appropriate selection of operating conditions. While watering the fatty acids may be accomplished at any time prior to their subjection to high heat, even before introducing them into the equipment, it is believed to be preferable to provide in the equipment for the dehydration of the fatty acids under atmospheric or subatmospheric pressure, followed by watering. It is also preferable to provide the equipment with variable speed pumps and to have the pressure control valve adjustable. These arrangements, together with temperature control of the furnace and the adjustable by-pass of the heat exchanger

which is located between the autoclave and the flash still, provide a flexibility which permits one piece of equipment to handle many types of raw material.

In any case, the size of the polymerization closure may be calculated to provide the lowest equipment cost for each unit of throughput which available construction materials permit, without regard to operating costs. This is made possible by the utilization of polymerization temperatures above those requisite for flash distillation and the reuse of the excess heat, whereby utilization of the low cost equipment entails no increased operating cost, save for radiation losses.

Having described my invention, I claim:

1. The method of removing polyunsaturated components as dimer acids from a mixture of fatty acids containing polyunsaturated fatty acids, said process comprising establishing a flowing stream of said mixed fatty acids, adding to said flowing stream substantially from one to five per cent water, heating said flowing stream to a temperature of from substantially 350° to 400° C., while maintaining a pressure sufficient to retain said water in solution in the fatty acids to inhibit decarboxylation of said fatty acids, holding said stream of fatty acids at said polymerizing temperature for a period of substantially twenty minutes to an hour, cooling said stream of fatty acids to substantially 260° to 360° C., releasing the pressure on said stream of fatty acids and flash distilling the unpolymerized components as distillate and recovering the polymerized components as a residue.

2. The method of heat treating a mixture of fatty acids containing polyunsaturants which comprises establishing a flowing stream of said fatty acids, adding water to said stream in amount sufficient to inhibit decarboxylation thereof during heating, and subjecting the fatty acids in said stream to a temperature of substantially 350° to 400° C., under a pressure of 300 to 600 lbs. per square inch pressure, for a period of time sufficient to effect polymerization of polyunsaturated components in said stream, and then cooling the stream and flash distilling unpolymerized components from it.

3. The method of heat treating a mixture of fatty acids containing polyunsaturants which comprises establishing a flowing stream of said fatty acids, adding water to said stream in amount sufficient to inhibit decarboxylation thereof during heating, and subjecting the fatty acids in said stream to a temperature of substantially 350° to 400° C., under a pressure of 300 to 600 lbs. per square inch pressure for a period of time sufficient to effect polymerization of polyunsaturated components in said stream, and then cooling the stream and flash distilling unpolymerized components from it, at an absolute pressure not substantially exceeding 10 millimeters of mercury.

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