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(54) Title: THE MANUFACTURE OF POLYASPARTIC ACIDS

(57) Abstract

Polyaspartic acid having a weight average molecular weight of 1000 to 5000 is produced by hydrolysis of anhydropolyaspartic acid. Anhydropolyaspartic acid is produced by condensation polymerization of L-aspartic acid. Greater than 80 % conversion is achievable utilizing "temperature vs time" profiles.

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THE MANUFACTURE OF POLYASPARTIC ACIDS

FIELD OF THE INVENTION

The present invention relates to a method of polymerizing aspartic acid and relates to polysuccinimides and polyaspartic acids.

BACKGROUND OF THE INVENTION

Polyaspartic acids have utility as calcium carbonate and calcium phosphate inhibitors. Their biodegradability makes them particularly valuable from the point of view of environmental acceptability and waste disposal.

Anhydropolyaspartic acids (i.e. polysuccinimides) are the anhydrous forms of polyaspartic acids.

Thermal condensation of aspartic acid to produce polyaspartic acid is taught by Etsuo Kokufuta, et al., "Temperature Effect on the Molecular Weight and the Optical Purity of Anhydropolyaspartic Acid Prepared by Thermal Polycondensation", Bulletin of the Chemical Society Of Japan, Vol. 51 (5), 1555-1556 (1978). Kokofuto teaches that the molecular weight of the polyaspartic acid produced by this method increases with increased reaction temperature. Moreover, the maximum percent conversion of the aspartic acid to anhydropolyaspartic acid suggested is no more than 68% using oil bath temperatures of between 325 °F and 425 °F.

A more recent work by Brenda J. Little et al, "Corrosion Inhibition By Thermal Polyaspartate" Surface Reactive Peptides and Polymers, pp 263-279, American Chemistry Society Symposium Series 444(1990), cited Kokofuto. Oil bath temperatures of 374 °F were used to

produce anhydropolyaspartic acid from powdered aspartic acid over a period of 24 to 96 hours. The results were no better than Kokofuto's.

SUMMARY

We have discovered how to produce a much higher percent conversion polyaspartic acid than has been taught or suggested by the prior art. Moreover, contrary to the teachings of the prior art, the molecular weight of the polyaspartic acid produced by our method does not increase with the reaction temperature.

We have discovered that the thermal condensation of powdered L-aspartic acid to produce polysuccinimide in high yields optimally occurs above the initiation temperature of about 370 °F and preferably occurs above 420 °F, and most preferably occurs above 440 °F.

A reactant temperature less than 370 °F may produce polysuccinimide over a period of many hours. Theoretical yields will be low; the conversion of the L-aspartic acid to polysuccinimide will be less than 70% and will require a period of many days.

As the reactant temperature increases above 370 °F, the percent conversion increases to greater than 90% and the reaction times become greatly reduced.

The thermal condensation of L-aspartic acid to polysuccinimide according the method of our invention produces a characteristically shaped "temperature vs. time" reaction curve. The curve is characterized by an initial, rapid rise in reactant temperature, followed by an endotherm signally the beginning of the reaction.

Immediately following the onset of the endotherm there is evaporative cooling, followed first by a temperature rise, and then by a second endotherm, which is followed by an evaporative cooling plateau. The temperature then rises to a plateau. That plateau is at a constant temperature. The reaction has gone to at least 95% conversion at the temperature midway between the final plateau and the time the temperature begins to rise to that plateau.

Polyaspartic acid is produced from the polysuccinimide by base hydrolysis.

The polyaspartic acid produced has a weight average molecular weight of 1000 to 5000. This molecular weight range is uniform regardless of the percent conversion.

The percent conversion of the L-aspartic acid to the polysuccinimide can be increased in reduced time periods by increasing the temperatures used.

Where the thermal fluid used to heat the L-aspartic acid is brought to 500 °F in a reasonable time period, at least 90% conversion can be effected within 4 hours.

Where the thermal fluid used to heat the L-aspartic acid is brought to a maintenance temperature of at least 550 °F within a reasonable time period, at least 90% conversion can be effected within 2 hours.

Continuous and batch processes can be used. Some process examples include fluidized bed; stirred reactor; and indirectly, heated rotary driers.

THE FIGURES

FIGURE 1 depicts a temperature versus time reaction curve. Series 1 is the oil temperature. Series 2 is the

reaction mixture temperature.

FIGURE 2 depicts a temperature versus time reaction curve. Series 1 is the oil temperature. Series 2 is the reaction mixture temperature.

FIGURE 3 depicts a temperature versus time reaction curve. Series 1 is the oil temperature. Series 2 is the reaction mixture temperature.

FIGURE 4 depicts a temperature versus time reaction curve. Series 1 is the oil temperature. Series 2 is the reaction temperature.

FIGURE 5 depicts a temperature versus time reaction curve. Series 1 is the oil temperature. Series 2 is the reaction temperature.

FIGURE 6 depicts a temperature versus time reaction curve. Series 1 is the oil temperature. Series 2 is the reaction mixture temperature.

FIGURE 7 depicts a temperature versus time reaction curve. Series 1 is the oil temperature. Series 2 is the reaction mixture temperature.

DISCUSSION

A series of experiments were conducted to thermally, polymerize solid phase L-aspartic acid. In each instance, the powdered L-aspartic acid was added to a reaction vessel and heated. Samples were taken throughout the polymerization reaction. Those samples were analyzed for percent conversion to the product, polysuccinimide, and the color and temperature of the samples were noted. The polysuccinimide was then hydrolyzed to produce polyaspartic

acid, and activity tests were conducted on the polyaspartic acid.

Each of these, conversion, color, production of polyaspartic acid, and activity are described below.

The following procedure was utilized to determine the percent conversion of the L-aspartic acid to the product, polysuccinimide:

THE DETERMINATION OF CONVERSION Of L - ASPARTIC ACID TO POLYSUCCINIMIDE

A specific amount of the reaction mixture or product was dissolved in an aliquot of dimethylformamide (DMF). The dissolution was allowed to proceed for 4 to 5 hours until all of the polysuccinimide dissolved in the DMF leaving unreacted L-aspartic acid which was filtered out. The amount of unreacted L-aspartic acid was determined by using the following formula:

$$\% \text{ CONVERSION} = \frac{A - B}{A} * 100\ \%$$

Where: A = weight of initial sample

B = weight of filtrate

COLOR

The color of each product sample was noted. The color of L-apsartic acid is white. The samples containing polysuccinimide varied in color according to the temperature of the sample taken from the reaction mixture. From low temperature to high, the colors varied as follows: light pink, to pink, to tannish pink, to tan, to light

yellow, to yellow. These colors generally corresponded to the percent conversion of the L-aspartic acid, in the same order with light pink indicating the lowest percent conversion and yellow indicating the highest percent conversion. The pink colors had less than 70 % conversion. The literature has never reported any other color but pink.

POLYASPARTIC ACID

Polyaspartic acid was produced from polysuccinimide using the following hydrolysis procedure:

Hydrolysis procedure for making polyaspartic acid from polysuccinimide.

A slurry was made from a measured amount of polysuccinimide and distilled water. Sodium hydroxide was added dropwise to hydrolyze polysuccinimide to polyaspartic acid. The completion of the hydrolysis was attained at pH 9.5.

Bases other than sodium hydroxide can be used. Suitable bases include ammonium hydroxide, potassium hydroxide, and other alkaline and alkaline earth hydroxides.

Generally, base should be added to the slurry until the pH has been raised to 9.5, and a clear solution has been formed.

ACTIVITY TEST

Polyaspartic acid was produced from the samples of polysuccinimide. The activity of the polyaspartic acid as an inhibitor for preventing the precipitation of calcium

carbonate was determined as described in the test below:

A standard volume of distilled water was pipetted into a beaker. Inhibitor was added after the addition of a calcium chloride solution, but prior to the addition of a solution of sodium bicarbonate. Sodium hydroxide was then added to the solution until there was an apparent and sudden calcium carbonate precipitation evidenced by the cloudiness of the solution.

At this point the pH dropped, the addition of the sodium hydroxide was stopped, and the pH was recorded. The volume of sodium hydroxide consumed was noted. The pH drop after ten minutes was recorded.

The amount of inhibitor used was adjusted to provide a constant weight of polyaspartic acid in each of the tests.

The activity of the inhibitor was judged by the volume of sodium hydroxide consumed and by the pH drop. The greater the amount of sodium hydroxide needed, the greater the activity of the product as an inhibitor. The smaller the pH drop, the greater the activity of the product as an inhibitor.

MOLECULAR WEIGHT DETERMINATION

Gel permeation chromatography was utilized to determine the molecular weights of the polyaspartic acid produced. The molecular weight determinations were made on the polysuccinimide that was hydrolyzed using the hydrolysis procedure described herein.

Rohm & Haas 2000 Mw polyacrylic acid and Rohm & Haas

4500 Mw polyacrylic acid were utilized as standards. The molecular weights provided for the polyaspartic acid produced according to this invention are based on these standards unless otherwise noted, and are reported as weight average molecular weights,(Mw). This is because molecular weights based on gel permeation chromatography can vary with the standards utilized.

It was found that the molecular weight for the polyaspartic acid produced fell within the range of 1000 Mw to 5000 Mw, regardless of percent conversion.

DEFINITIONS

The term polyaspartic acid used herein also includes salts of polyaspartic acid. Counterions for polyaspartate include, but are not limited to, the alkaline and alkaline earth cations, some examples of which are Na^+, K^+, Mg^+, and Li^+, Ca^{++}, Zn^{++}, Ba^{++}, Co^{++}, Fe^{++}, Fe^{+++}, and $NH4^+$.

Polysuccinimide is the imide form of polyaspartic acid and is also known as anhydropolyaspartic acid.

Conversion is defined to be the degree to which L-aspartic acid has formed polysuccinimide by thermal condensation.

Equilibrium temperature is defined to be the temperature of the product upon completion of the reaction.

EXPERIMENTS

Reported below are examples of the production of polysuccinimide and polyaspartic acid.

Laboratory Experiment 1

A "time vs. temperature" plot of the following reaction is depicted in Figure 1.

A 500 ml covered, stainless steel, beaker charged with 400 grams of powdered L-aspartic acid was placed in an oil bath. The oil bath was quickly heated to a 425 °F maintenance temperature. The sample was stirred throughout the experiment.

At 40 minutes, the reaction began when the first endotherm was reached. The first endotherm of the reaction mixture peaked at 390 °F at an oil temperature of 425 °F which was the maintenance temperature.

Evaporative cooling immediately followed this first endotherm. Water loss was evidenced by the evolution of steam. The reaction mixture temperature dropped to a low of 360 °F during this period. Following the temperature drop, the reaction mixture began to heat up. At 2.75 hours, the reaction mixture attained a plateau temperature of 400 °F. At the end of 6.88 hours, 42 percent conversion had been attained. Steam coming from the system evidenced water loss throughout the entire endothermic reaction. Evaporative cooling still continued to take place. The experiment was concluded after the seven hour experiment.

Table 1 below provides data developed during this experiment. Samples were taken at the times indicated and analyzed for percent conversion to polysuccinimide.

The relative activity of polyaspartic acid produced from the the product polysuccinimide was determined by the activity test described above. Activity is reported in terms of pH drop (δpH) and milliliters (mls) of sodium hydroxide, as described in the Activity test.

The color of the reaction mixture is provided. Color

was observed to vary with product temperature.

TABLE 1

POLYMERIZATION				ACTIVITY TEST		
Time	Product	Oil	Conv	NaOH	δpH	Color
hr	°F	°F	%	ml		
0.0	250	270	0	0.95	1.47	LP
1.0	386	430	5	----	----	LP
1.7	385	425	13	1.75	0.56	P
3.4	401	425	26	1.75	0.56	P
5.0	400	424	27	1.75	0.56	P
6.9	400	425	42	1.80	0.57	P

The following definitions apply through out this writing: LP = light pink; LY = light yellow; P = Pink; T = Tan; W = White; Y = Yellow; Conv = Conversion; δpH = activity test pH drop; hr = hours

Laboratory Experiment 2

A "time vs. temperature" plot of the following reaction is depicted in Figure 2.

A 500 ml covered, stainless steel, beaker charged with 400 grams of powdered, L-aspartic acid was placed in an oil bath. The oil bath was quickly heated to a 450 °F maintenance temperature. The sample was stirred throughout the experiment.

At 30 minutes, the reaction began when the first endotherm was reached. The first endotherm of the reaction mixture peaked at 395 °F at an oil temperature of 439 °F.

Evaporative cooling immediately followed this first endotherm. Water loss was evidenced by the evolution of steam. The reaction mixture temperature dropped to a low of 390 °F during this period and the oil temperature rose to the 450 °F maintenance temperature. Following the temperature drop, the reaction mixture began to heat up. At 1.67 hours, a second endotherm occurred. At this endotherm, the reaction mixture temperature was 420 °F and the oil temperature was 450 °F. Steam coming from the system evidenced water loss.

Evaporative cooling continued to take place until the conclusion of the second endotherm. Water loss was evidenced by the evolution of steam.

At the conclusion of this period, the reaction mixture was then heated up and maintained at an equilibrium temperature of 434 °F.

Table 2 below provides data developed during this experiment. Samples were taken at the times indicated and analyzed for percent conversion to polysuccinimide.

The relative activity of polyaspartic acid produced from the the product polysuccinimide was determined by the activity test described above. Activity is reported in terms of pH drop (δpH) and milliliters (mls) of sodium hydroxide, as described in the activity test.

The color of the reaction mixture is provided. Color was observed to vary with product temperature.

TABLE 2

POLYMERIZATION				ACTIVITY TEST		
Time	Product	Oil	Conv	NaOH	δpH	
Color						
hr	°F	°F	%	ml		
0.0	340	345	0	0.95	1.47	W
0.5	400	440	22	----	---	LP
1.1	396	451	23	1.75	0.59	LP
1.7	422	457	32	1.80	0.57	P
4.2	416	451	58	1.81	0.61	P
5.5	420	452	81	1.80	0.63	T
7.1	430	454	97	1.75	0.69	T

Laboratory Experiment 3

A "time vs. temperature" plot of the following reaction is depicted in Figure 3.

A 500 ml covered, stainless steel, beaker charged with 400 grams of powdered, L-aspartic acid was placed in an oil bath. The oil bath was quickly heated to a 500 °F maintenance temperature. The reaction mixture was stirred throughout the experiment.

At 30 minutes, the reaction began when the first endotherm was reached. The first endotherm of the reaction mixture peaked at 405°F at an oil temperature of 465 °F.

Evaporative cooling immediately followed the first endotherm. Water loss was evidenced by the evolution of steam. The reaction mixture temperature dropped to a low

of 390 °F during this period, and the oil temperature rose to 490 °F.

At 1.25 hours, a second endotherm occurred. At this second endotherm, the reaction mixture temperature was 438 °F and the oil temperature was 495 °F.

Evaporative cooling continued to take place until the conclusion of the second endotherm. Water loss was evidenced by the evolution of steam. The reaction mixture temperature dropped to a low of 432 °F during this period and the oil temperature rose to 599 °F.

A diminution in evaporative cooling was evidenced by a steady rise in reaction mixture temperature between approximately 2.65 hours and 3.17 hours. At 3.17 hours a temperature plateau was attained. No further increase in conversion was noted beyond that point.

Table 3 below provides data developed during this experiment. Samples were taken at the times indicated and analyzed for percent conversion to polysuccinimide.

The relative activity of polyaspartic acid produced from the the product polysuccinimide was determined by the activity test described above. Activity is reported in terms of pH drop (δpH) and milliliters (mls) of sodium hydroxide, as described in the activity test.

The color of the reaction mixture is provided. Color was observed to vary with product temperature.

TABLE 3

POLYMERIZATION				ACTIVITY TEST	
Time	Product	Oil	Conv	NaOH	δpH
Color					
hr	°F	°F	%	ml	
0.0	256	316	0	0.95	1.47 W
0.5	406	464	7	----	---- LP
1.3	437	496	43	1.80	0.56 P
2.3	438	497	81	1.80	0.56 P
3.1	470	499	90	1.80	0.67 TP
3.8	476	500	95	1.80	0.63 TP
6.0	476	502	98	1.80	0.63 LY

Laboratory Experiment 4

A "time vs. temperature" plot of the following reaction is depicted in Figure 4.

A 500 ml covered, stainless steel, beaker charged with 400 grams of powdered, L-aspartic acid was placed in an oil bath. The oil bath was quickly heated to a 550 °F maintenance temperature. The sample was stirred throughout the experiment.

At 24 minutes, the reaction began when the first endotherm was reached. The first endotherm of the reaction mixture peaked at 410°F at an oil temperature of 470 °F.

Evaporative cooling immediately followed the first endotherm. Water loss was evidenced by the evolution of steam. The reaction mixture temperature dropped to a low

of 395 °F during this period.

A second endotherm occurred at 1 hour at a reaction mixture temperature of 442 °F.

Evaporative cooling continued to take place until the conclusion of the second endotherm. The reaction mixture temperature dropped to a low of 440 °F during this period.

A diminution in evaporative cooling was evidenced by a steady rise in reaction mixture temperature between approximately 1.5 hours and 2.06 hours. At 2.06 hours a temperature plateau was attained. No further increase in percent conversion was noted beyond 1.95 hours.

Table 4 below provides data developed during this experiment. Samples were taken at the times indicated and analyzed for percent conversion to polysuccinimide.

The relative activity of polyaspartic acid produced from the the product polysuccinimide was determined by the activity test described above. Activity is reported in terms of pH drop (δpH) and milliliters (mls) of sodium hydroxide, as described in the activity test.

The color of the reaction mixture is provided. Color was observed to vary with product temperature.

TABLE 4

POLYMERIZATION				ACTIVITY TEST		
Time hr	Product °F	Oil °F	Conv %	NaOH ml	δpH	Color
0.0	330	348	0	0.95	1.47	W
0.5	405	470	11	----	----	LP
1.0	436	520	36	1.80	0.60	LP
1.4	439	536	66	1.80	0.67	P
1.8	462	540	92	1.80	0.58	TP
2.0	495	544	94	1.75	0.64	TP
2.4	510	547	96	1.75	0.58	LY
3.4	512	548	98	1.80	0.63	Y

Production scale product runs were conducted as follows:

Pilot Plant Test Run #1

A "time vs. temperature" plot of the following reaction is depicted in Figure 5.

A DVT-130 drier, mixer manufactured by the Littleford Brothers, Inc., of Florence, Kentucky was used. The jacketed drier utilizes a thermal fluid (hereinafter called "oil"), a plough blade impeller, a stack open to the atmosphere; and has a heat transfer area of 10 ft^2. The reactor's oil reservoir was preheated to 550 °F.

The reactor was charged with 110.4 lb of powdered, L-aspartic acid. Hot oil began to flow through the jacket, and the impeller speed was set at 155 rpm. Both the product and oil temperatures rose steadily. At a product temperature of 390 °F, there was a sudden, endothermic reaction which caused the product temperature to drop (see

Fig. 5). Water loss was evidenced by the evolution of steam. A sample taken revealed that the powder had changed from white to pink. Three percent of the material was converted to polysuccinimide.

Thereafter, product temperature began to rise steadily until it reached a plateau at 428 °F which continued for an hour. Throughout this whole reaction, steam evolved, and the conversion increased in a linear fashion. At the end of the hour, the product temperature rose to 447 °F at which time the reaction underwent a second endotherm. Immediately after this endotherm, steam ceased to evolve. Shortly after this point, the reaction was at least 88% complete. Following the second endotherm, the product slowly changed from a pink to a yellow color. The final conversion was measured at 97%.

Table 5 below provides data developed during this experiment. Samples were taken at the times indicated and analyzed for percent conversion to polysuccinimide.

TABLE 5

POLYMERIZATION			
Time	Product	Oil	Conv
hr	°F	°F	%
0.0	70	375	0
0.8	390	394	3
1.1	396	504	15
1.5	423	501	24
2.0	430	500	41
2.6	430	506	61
3.6	444	505	84
4.5	471	508	88
5.8	466	506	97

Pilot Plant Test Run #2

A "time vs. temperature" plot of the following reaction is depicted in Figure 6.

A Littleford DVT-130 drier, mixer with a heat transfer area of 10ft², was charged with 110.4 lb of powdered, L-aspartic acid, and the oil reservoir was preheated to 525 °F.

At the start up, hot oil began to flow through the jacket, and the impeller speed was set at 155 rpm. Both the product and oil temperatures rose steadily. The product temperature rose to 393 °F whereupon a sudden, endothermic reaction caused the product temperature to drop (see Fig. 6) and steam began to evolve. A sample taken

revealed that the powder had changed from white to pink. Four percent of the material was converted to polysuccinimide. Thereafter, product temperature began to rise steadily until it reached a plateau at 427 °F which continued for one and a half hours. Throughout this whole reaction, steam was evolved, and the conversion increased in a linear fashion. At the end of this time, the product temperature rose to 444 °F until the reaction underwent a second endotherm. Immediately after this second endotherm, steam ceased to evolve. Shortly after this point, the reaction was at least 94% complete. Following the second endotherm, the product slowly changed from a pink to a yellow color. The final conversion was measured at 98%.

Table 6 below provides data developed during this experiment. Samples were taken at the times indicated and analyzed for percent conversion to polysuccinimide.

TABLE 6

POLYMERIZATION			
Time	Product	Oil	Conv
hr	°F	°F	%
0.0	70	400	0
1.0	393	488	5
1.3	400	476	18
2.0	428	475	20
3.9	441	480	66
4.4	450	477	85
5.1	456	476	94
6.1	457	484	98

Pilot Plant Test Run #3

A "time vs. temperature" plot of the following reaction is depicted in Figure 7.

A " B" blender, manufactured by J.H. Day of Cincinatti, Ohio was charged with 110.4 lb of powdered, L-aspartic acid. The unit was a trough-shaped blender with a plough-bladed impeller and a heat transfer area of approximately 8 ft^2. The reactor was wrapped in fiberglass insulation because the oil heater was undersized. The reactor also had a large funnel in a top port open to the atmosphere. The oil reservoir was preheated to 500 °F. At the start up, hot oil began to flow through the jacket, and the impeller began to rotate at 74 rpm. Both the

product and oil temperatures rose steadily. The product temperature rose to 377 °F whereupon a sudden, endothermic reaction caused the product temperature to drop (see Fig. 7) and steam began to evolve. A sample taken revealed that the powder had changed from white to pink. Thirteen percent of the material was converted to polysuccinimide. Thereafter, product temperature began to rise steadily until it reached a plateau at 416 °F which continued for 3.75 hours. Throughout this whole reaction, steam was evolved, and the conversion increased in a linear fashion. Due to the heater being undersized, it took a longer time for the product temperature to rise. At the end of this time, the product temperature rose to 435 °F. The reaction was at least 88% complete. Due to time limitations, the reaction was stopped when the product temperature reached the plateau. At this point, the final conversion was measured at 90%.

Table 7 below provides data developed during this experiment. Samples were taken at the times indicated and analyzed for percent conversion to polysuccinimide.

TABLE 7

POLYMERIZATION			
Time	Product	Oil	Conv
hr	°F	°F	%
0.0	55	390	0
1.0	370	420	0
2.3	377	448	13
3.0	403	455	21
3.5	416	460	26
4.0	417	469	32
4.5	416	471	38
5.0	416	472	45
5.5	415	460	52
6.8	413	446	64
7.3	414	448	70
7.8	418	451	74
8.3	422	455	81
9.3	433	460	88
9.8	435	460	90

The experiments show that degree of conversion of L-aspartic acid and the time required for conversion is related to the temperature of the reaction mixture.

The higher the temperature of the thermal fluid used to heat the reaction mixture, the higher the degree of polymerization and the faster the rate of conversion.

Because of normal heat losses the temperature of the

thermal fluid will always be higher than the temperature of the reaction mixture. It is known that increasing the temperature of the thermal fluid will increase the driving force of the reaction. Assuming that the thermal fluid temperature will be raised to its maintenance temperature in a reasonably short period of time, we have found that generally the following has held true:

Where the oil maintenance temperature was 425 °F, at the end of 5 days only 60% conversion was achieved. The equilibrium temperature of the reaction mixture appeared to be 400 °F.

Where the oil maintenance temperature was 450 °F, 90% conversion took place within 7 hours. The equilibrium temperature of the reaction mixture is not known.

Where the oil maintenance temperature was 500 °F, 90% conversion took place within 4 hours. The equilibrium temperature of the reaction mixture was 477 °F.

Where the oil maintenance temperature was 550 °F, 90% conversion took place within 2 hours. The equilibrium temperature of the reaction mixture was 510 °F.

The difference between the maintenance temperature and the reaction temperatures provides the driving force. Different means for providing the thermal energy can result in different driving forces. Thus, although the relations derived here are qualitatively valid, there may be some quantitative differences found in different systems. Different thermal resistances will result in a shift in temperature and/or time requirements.

The systems tested here tend to have high thermal

resistance. For systems with less thermal resistance, lower source temperatures will suffice to provide equivalent results.

The data indicates that continuous as well as batch processes can be used. The relationships we have just discussed are equally valid for both. Based on the data presented herein, a number of different reactors can be used. Examples of these include, but are not limited to a heated rotary drier; a stirred reactor; a fluidized bed and the like. The reaction can occur at ambient pressure or under a vacuum. The reaction can occur in air or a variety of atmospheres, inert or otherwise.

As a further example, an indirectly heated rotary drier having the same residence time as for example the DVT 130, would provide similar results under the same operating conditions.

Having described our invention, we claim as follows:

1). A method for producing polysuccinimide, comprising the steps of

a). heating powdered L-aspartic acid to at least 370 °F to initiate the condensation reaction, then

b). raising the reaction mixture temperature to at least 420 °F, and

c). maintaining at least the 420 °F temperature until at least 80% conversion has occurred.

2). The method of claim 1, wherein the reaction mixture temperature is raised to at least 430 °F for a period of time sufficient to effect at least 90 % conversion.

3). The method of claim 1, wherein the reaction mixture temperature is raised to at least 440 °F for a period of time sufficient to effect at least 95% conversion.

4). The method of claim 1, further including the step of mixing the reaction mixture during the process of producing polysuccinimide for the purpose of facilitating heat transfer to the reactants.

5). The method of claim 2, further including the step of mixing the reaction mixture during the process of producing polysuccinimide for the purpose of facilitating heat transfer to the reactants.

6). The method of claim 3, further including the step of mixing the reaction mixture during the process of producing polysuccinimide for the purpose of facilitating heat transfer to the reactants.

7). The process of hydrolyzing the product of claim 2 with a base.

8). The product made according to the process of claim 7 having a weight average molecular weight within the range of 1000 to 5000, regardless of the percent conversion.

9). The method of claim 2, further including the step of hydrolyzing the product of claim 4 with a base.

10). The product made according to the process of claim 9, having a weight average molecular weight within the range of 1000 to 5000, regardless of the percent conversion.

11). The method of claim 3, further including the step of hydrolyzing the product of claim 3 with a base.

12). The product made according to the process of claim 11, having a weight average molecular weight within the range of 1000 to 5000, and having a uniform activity regardless of percent conversion.

13). A method of producing polysuccinimide, wherein a thermal fluid used to heat L-aspartic acid is brought to a maintenance temperature of at least 500 °F within a reasonable period of time, to effect at least 90% conversion within 4 hours.

14). The method of claim 13, further including the step of hydrolyzing the polysuccinimide produced using a base to produce a polyaspartic acid having a weight average molecular weight within the range of 1000 to 5000.

15). The method of Claim 13, wherein the thermal fluid is brought to a maintenance temperature of at least 550 °F to effect at least 90% conversion within 2 hours.

16). The process claim 15, further including the step of hydrolyzing the polysuccinimide produced with a base to produce polyaspartic acid having a weight average molecular

weight within the range of 1000 to 5000.

17). A polyaspartic acid, produced by the process of

a). mixing solid L-aspartic acid to attempt to establish a relatively uniform temperature throughout,

b). heating the solid L-aspartic acid to a temperature of at least 375 °F to initiate a condensation reaction,

c). raising the temperature until a temperature of at least 420 °F is attained substantially throughout the reaction mixture, and

d). base hydrolyzing the polysuccinimide produced in steps b and c, to produce a polyaspartic acid;

the polyaspartic produced uniformly having a weight average molecular weight within the range of 1000 to 5000, regardless of the percent conversion.

18). A method of producing polysuccinimide, comprising the steps

a). introducing powdered L-aspartic acid to a indirectly, heated rotary drier;

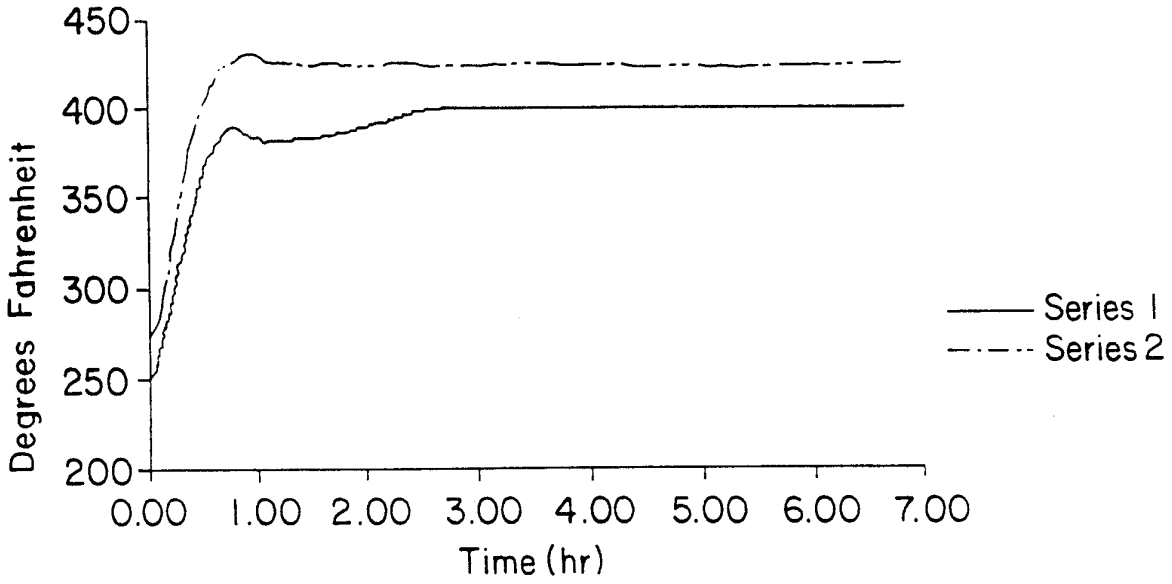
b). heating the powdered L-aspartic acid rapidly to a temperature of at least 370 °F to initiate the condensation reaction;

c). rapidly raising the temperature to at least 440 °F; and

d). maintaining at least the 440 °F temperature until at least 80% conversion has been achieved.

19). A method of producing polyaspartic acid, comprising base hydrolyzing the polysuccinimide produced in claim 18.

FIG. 1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Degrees Fahrenheit
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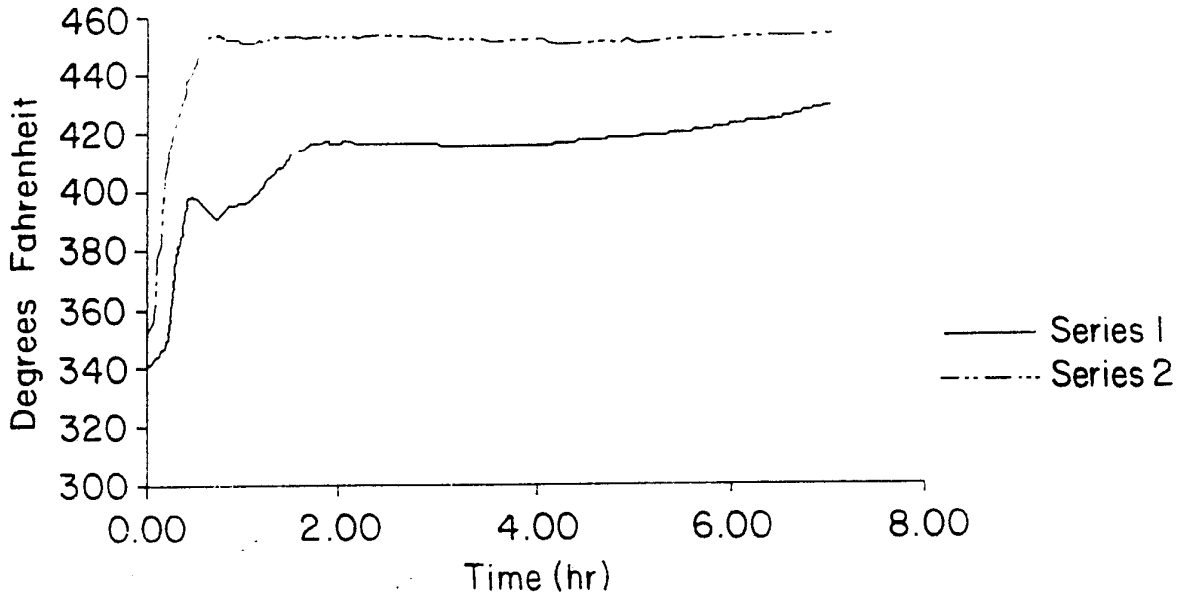
Time (hr)
Series 1
Series 2

FIG. 2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Time (hr)
Series 1
Series 2

FIG. 3

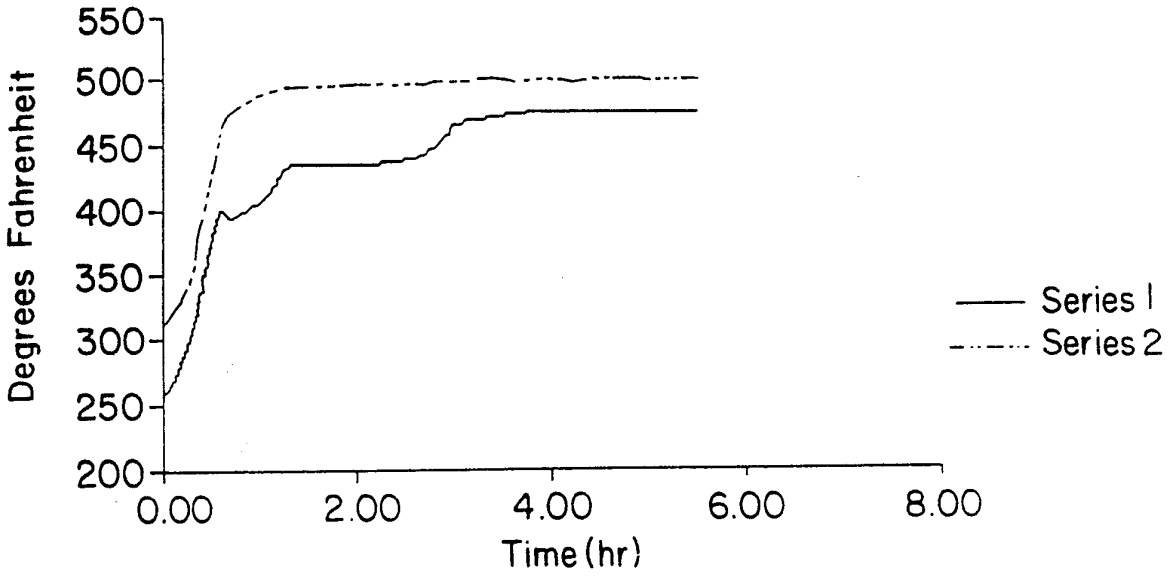
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FIG. 4

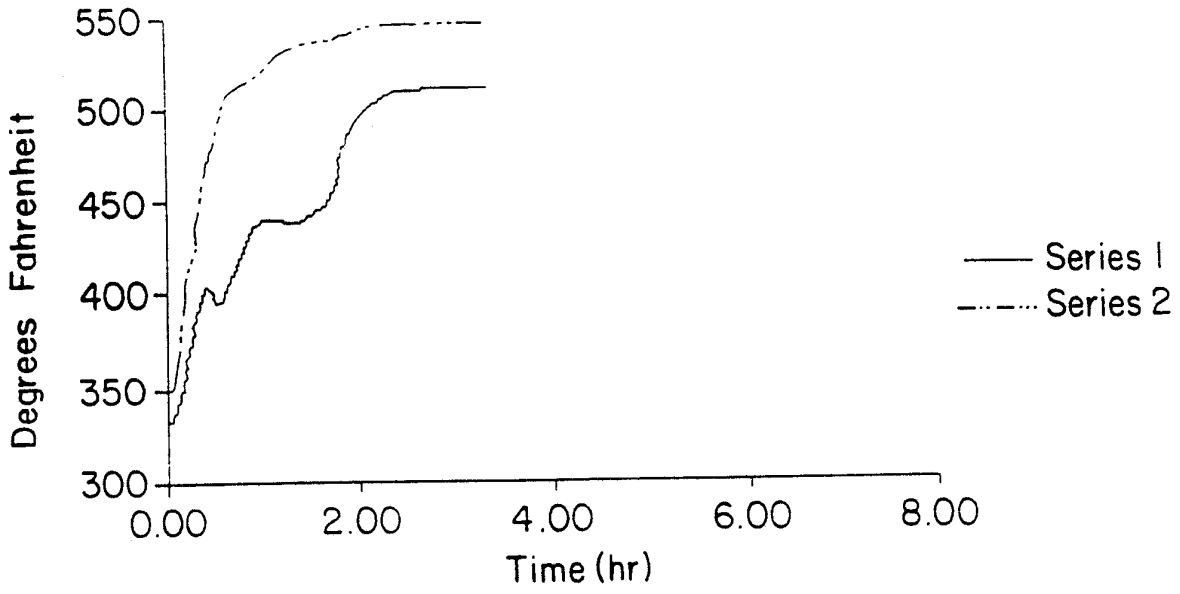
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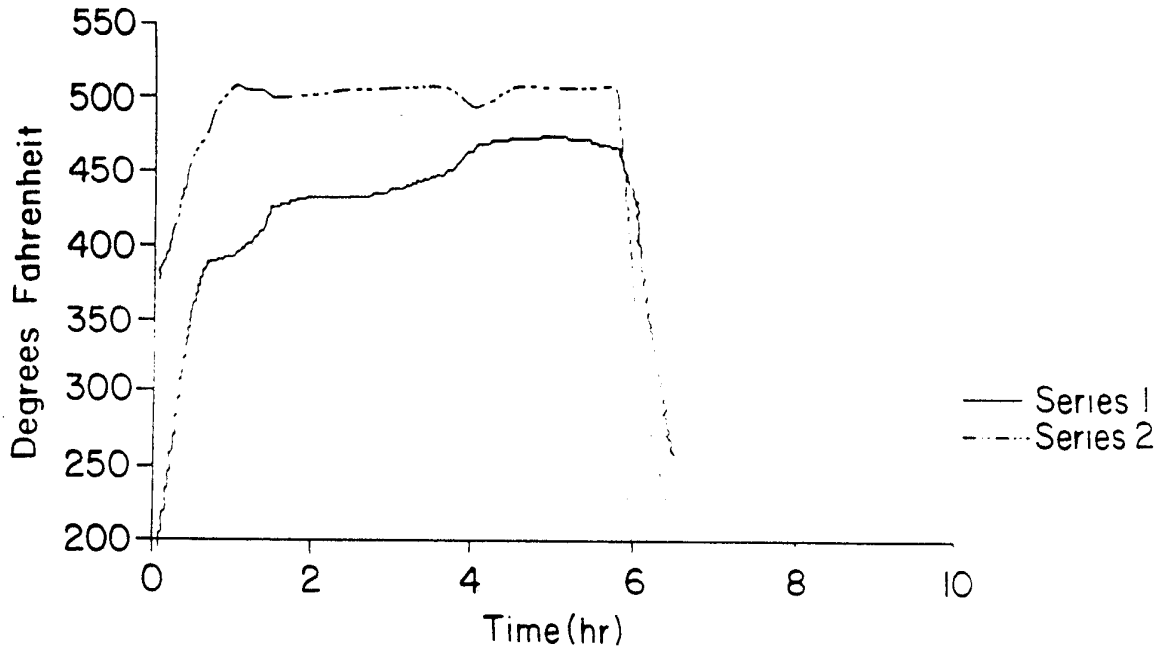
FIG. 5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Time (hr)
Series 1
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FIG. 6

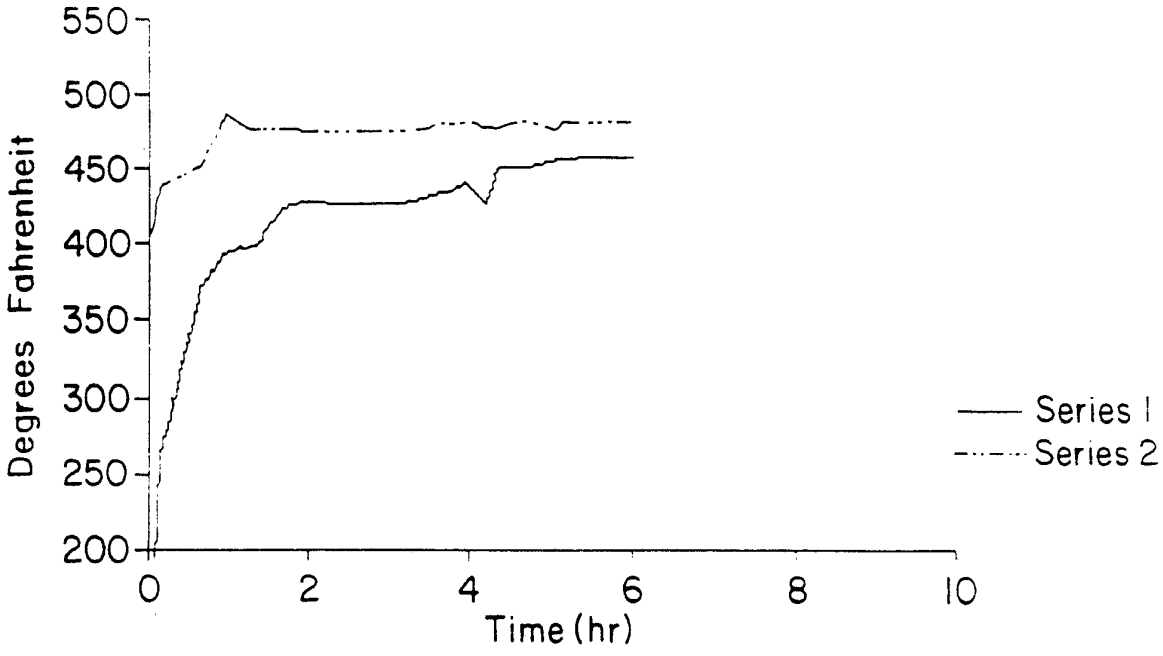
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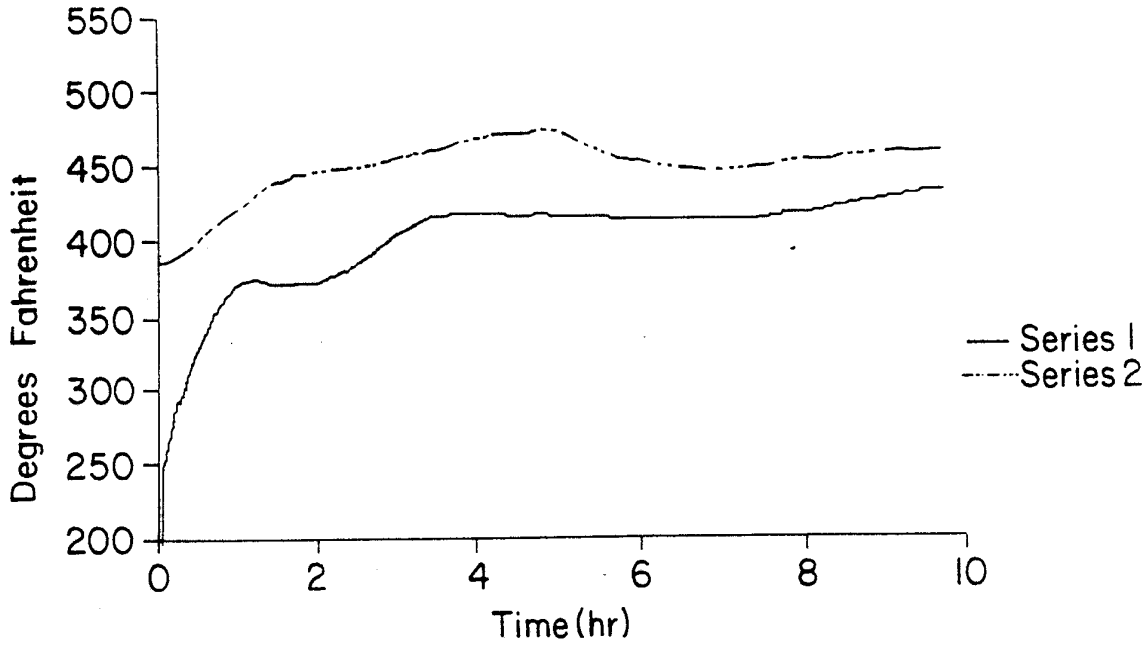
FIG. 7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Time (hr)
Series 1
Series 2

INTERNATIONAL SEARCH REPORT

International Application No. PCT/US92/01389

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[3]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC (5): C07K 7/10
US CL : 530/324, 339, 343, 345

II. FIELDS SEARCHED

Minimum Documentation Searched[4]

Classification System	Classification Symbols
U.S.	530/324, 339, 343, 345

Documentation Searched other than Minimum Documentation to the extent that such Documents are included in the Fields Searched[5]

APS TEXT SEARCH

III. DOCUMENTS CONSIDERED TO BE RELEVANT[14]

Category*	Citation of Document,[16] with indication, where appropriate, of the relevant passages[17]	Relevant to Claim No.[18]
X	BIOPOLYMERS, VOL. 20, ISSUED 1981, V. SAUDEK ET AL., "NMR STUDY OF POLY(ASPARTIC ACID)", PAGES 1614-1622, SEE ENTIRE DOCUMENT.	1-19
X	AMERICAN CHEMICAL SOCIETY, VOL. 97, CHAPTER 21, ISSUED 1991, B.J. LITTLE ET AL., "CORROSION INHIBITION BY THERMAL POLYASPARTATE", PAGES 263-279, SEE PAGES 263-264.	1-19
X	BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 51, NO. 5, ISSUED 1978, E. KOKUFUTA ET AL., "TEMPERATURE EFFECT ON THE MOLECULAR WEIGHT AND THE OPTICAL PURITY OF THE ANHYDRO POLYASPARTIC ACID PREPARED BY THERMAL POLYCONDENSATION", PAGES 1555-1556, SEE ENTIRE BULLETIN.	1-19

* Special categories of cited documents:[15]

"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier document but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search[2]	Date of Mailing of this International Search Report[2]
19 MAY 1992	01 JUN 1992
International Searching Authority[1]	Signature of Authorized Officer[20]
ISA/US	LESTER L. LEE