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(72) Inventeurs/Inventors:
KOSKAN, LARRY P., US;
LOW, KIM C., US

(73) Propriétaire/Owner:
DONLAR CORPORATION, US

(74) Agent: CASSAN MACLEAN

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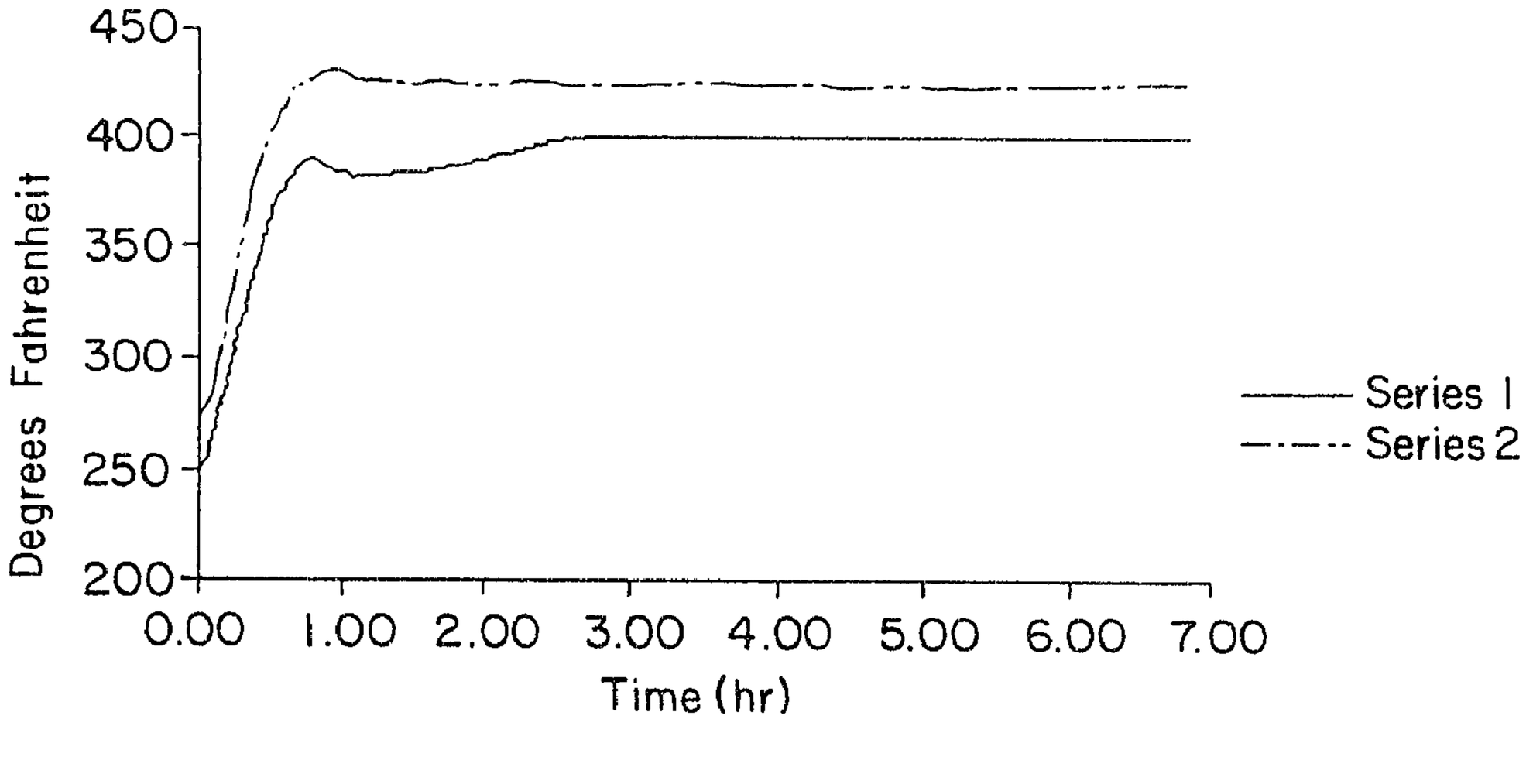
(54) Title: POLYASPARTIC ACID AS A CALCIUM SULFATE AND A BARIUM SULFATE INHIBITOR



(57) Abrégé/Abstract:
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(71) Applicant: DONLAR CORPORATION [US/US]; 400 East Sibley Blvd., Harvey, IL 60426 (US).

(72) Inventors: KOSKAN, Larry, Paul ; 8617 Golfview Drive, Orland Park, IL 60462 (US). LOW, Kim, C. ; 4646 West 122nd Street, Apartment 303, Alsip, IL 60658 (US).

(74) Agent: CUPOLI, Anthony, L.; 37 Peppertree Drive, Palatine, IL 60067-2703 (US).

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(54) Title: POLYASPARTIC ACID AS A CALCIUM SULFATE AND A BARIUM SULFATE INHIBITOR

(57) Abstract

Polyaspartic acid as a calcium sulfate and barium sulfate inhibitor. Generally all forms of polyaspartic acid can be used. β-polyaspartic acids are preferred.

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POLYASPARTIC ACID AS A CALCIUM SULFATE AND A BARIUM SULFATE INHIBITOR

FIELD OF THE INVENTION

The present invention relates to a method of using polyaspartic acid to inhibit the precipitation of calcium sulfate and barium sulfate.

BACKGROUND OF THE INVENTION

Calcium sulfate and barium sulfate inhibitors are used in a number of industrial applications to prevent precipitation and scale formation. Included among these are cooling water treatment, boiler water treatment, desalination, reverse osmosis, flash evaporators, and oil field recovery operations.

The biodegradability of polyaspartic acids makes them particularly valuable from the point of view of environmental acceptability and waste disposal. After polyaspartic acid has been utilized, it biodegrades to environmentally acceptable end products.

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).

Koaru Harada et al, U.S. Patent number 4,696,981 teaches the use of microwaves to produce anhydropolyaspartic acid from microwave irradiation of monoammonium, diammonium, monoamide, diamide and monoamideammonium salts of malic acid, maleic acid, fumaric acid and mixtures of these. Production of polyaspartic acid by partial hydrolysis of the anhydropolyaspartic acid with aqueous sodium bicarbonate is taught.

Other methods for producing polyaspartic acid are known. A number of these are referenced in U. S. Patent number 4,543,881. That patent teaches the use of certain polyaspartic acids for calcium carbonate inhibition.

It is also known that certain polyaspartic acids inhibit calcium phosphate crystallization. See " Inhibition of Calcium Carbonate and Phosphate Crystallization by Peptides Enriched in Aspartic Acid and Phosphoserine," by Sikes et al, ACS Symposium Series 444 (1991), pages 50-71.

SUMMARY

Koskan, L. P. and Low, K. C., in a concurrently filed application entitled "Polyaspartic Acid as a Calcium Carbonate and a Calcium Phosphate Inhibitor" further disclose a method of inhibiting calcium carbonate and calcium phosphate that significantly improves inhibition by an improved composition of polyaspartic acid. That application is not to be considered prior art.

No one has reported using polyaspartic acids for calcium sulfate or barium sulfate inhibition. We have discovered that the precipitation of calcium sulfate and barium sulfate in aqueous systems can be inhibited with polyaspartic acid. The term polyaspartic acid includes the salts of polyaspartic acid.

Any polyaspartic acid will work. A preferred polyaspartic acid in ß-polyaspartic acid (i.e. one having >50% ß and <50% α form). Preferrably, the ß-polyaspartic acid is in having 60-80% ß-form, and a Mw within the range of 1000 to 5000. More preferrably, the polyaspartic acid is approximately 70% to 80% ß, and has an Mw within the range of 3000 to 5000. Most preferrably, the polyaspartic acid is approximately 70-75% ß, and has a Mw within the range of 3000 to 5000.

The ß-polyaspartic acid can be produced by the steps of heating powdered L-aspartic acid to at least 370 °F to initiate a condensation reaction , then raising the reaction mixture temperature to at least 420 °F, maintaining at least the 420 °F until at least 80% conversion to

polysuccinimide has occurred, and hydrolyzing the polysuccinimide.

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 or carbonates.

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

CALCIUM SULFATE 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 sulfate 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 sulfate. After the addition of sodium sulfate, the solution was mixed until precipitation occurred. The amount of precipitated calcium sulfate was filtered, dried and weighed.

The amount of inhibitor used was adjusted to provide a constant weight of polyaspartic acid in each of the tests. The smaller the amount of precipitated calcium sulfate, the better the inhibitor.

The table below, provides a summary of the test results.

TABLE A

Inhibitor	Concentration(ppm)	Weight of Precipitate(g)
Control	0	1.51
Polyaspartic Acid	10	1.30
Polyacrylic Acid**	10	1.38
Polyaspartic Acid	100	0
Polyacrylic Acid **	100	0.96
Polyaspartic Acid	200	0
Polyacrylic Acid**	200	0.6

**Polyacrylic Acid is from Rohm & Haas, 4500 Mw.

BARIUM SULFATE ACTIVITY TEST

A solution of barium chloride was added to distilled water containing a selected concentration of inhibitor. Sodium sulfate was then added and the mixture was stirred. A white precipitate of barium sulfate formed and turbidity was measured. The lesser the turbidity (NTU), the better the inhibitor. Results are reported in Table B below.

TABLE B

Concentration*	Polyaspartic Acid	Polyacrylic Acid**
ppm	NTU	NTU
1	156	117
10	12	28
200	7	18
1000	7	16

*Inhibitor concentration

**Polyacrylic Acid is from Rohm & Haas, 4500 Mw.

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.

ß COMPOSITION

The polyaspartic acid prepared according to the procedures described in laboratory experiments 1-4 and pilot plant test runs 1-3 under the heading "EXPERIMENTS" can be termed ß-polyaspartic acid, since NMR studies show it contains greater than 50% 3-carboxypropionamide, and less than 50% 2-acetoacetamide.

The polyaspartic acid produced was a copolymer containing two forms of L-aspartic acid. The α form is 2-acetoacetamide. The ß form is 3-carboxypropionamide.

An nmr was conducted on two different product samples. One sample had 70% ß form; the other had 75% ß form. It is believed that by varying the strength of the caustic used to hydrolyze anhydropolyaspartic acid, greater or lesser percentages of ß can be achieved.

The polyaspartic acid exemplifying this invention have greater than 50% ß and less than 50% α form. Preferably, the polyaspartic acids produced by this method are approximately 65% to 80% ß and 20% to 35% α polyaspartic acid. More preferably, they are 70% to 80% ß and most preferably they are 70% to 75% ß.

POLYASPARTIC ACID PRODUCT

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.

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 product polysuccinimide was determined by the calcium carbonate 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 product polysuccinimide was determined by the calcium carbonate 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 product polysuccinimide was determined by the calcium carbonate 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 product polysuccinimide was determined by the calcium carbonate 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	Product	Oil	Conv	NaOH	δpH	Color
hr	°F	°F	%	ml		
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 Cincinnati, 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.

WE CLAIM:

1. A method of inhibiting the precipitation of calcium sulfate or barium sulfate in an aqueous system, which comprises treating the aqueous system with a sulfate inhibiting amount of β-polyaspartic acid.

2. The method of claim 1, wherein the polyaspartic acid has a weight average molecular weight within the range of 1000-15000.

3. The method of claim 1, wherein the polyaspartic acid was produced by

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

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

(c) maintaining the reaction mixture at a temperature of at least 420°F until at least 80% conversion to polysuccinimide has occurred, and

(d) thereafter hydrolyzing the polysuccinimide.

CASSAN MACLEAN
Suite 401, 80 Aberdeen Street
Ottawa, Ontario
K1S 5R5

Agents for the Applicant

2083390

FIG. 1

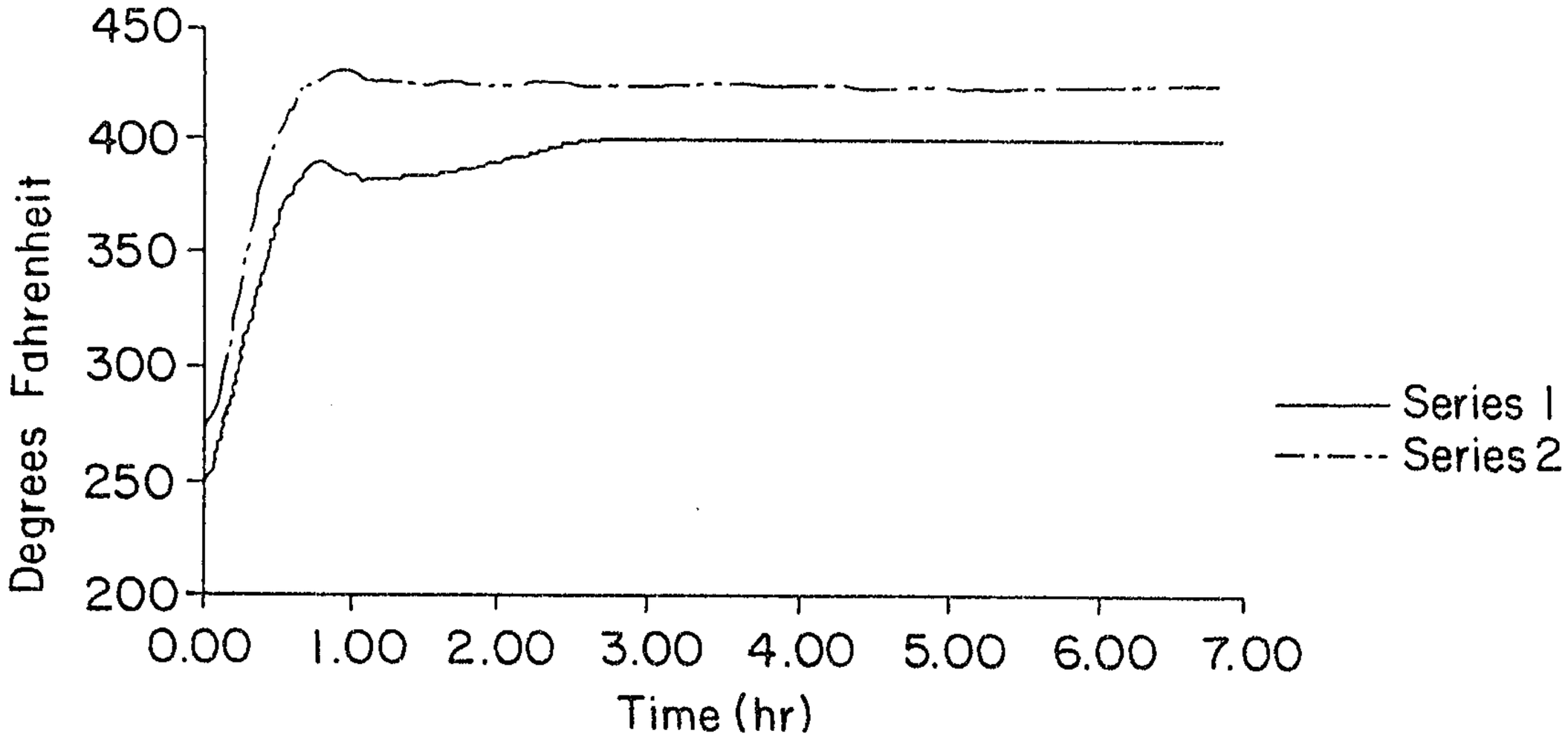


FIG. 2

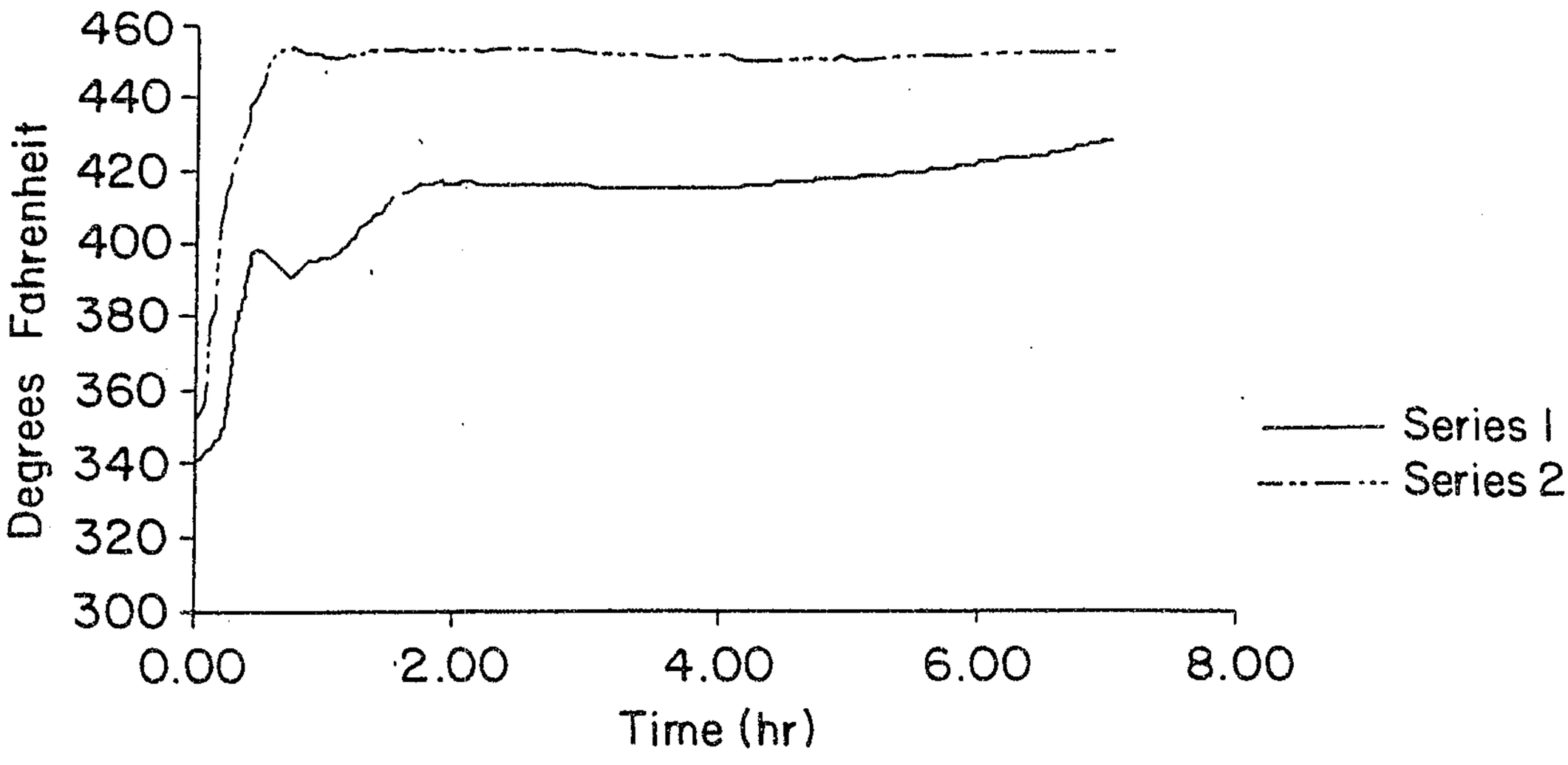


FIG. 3

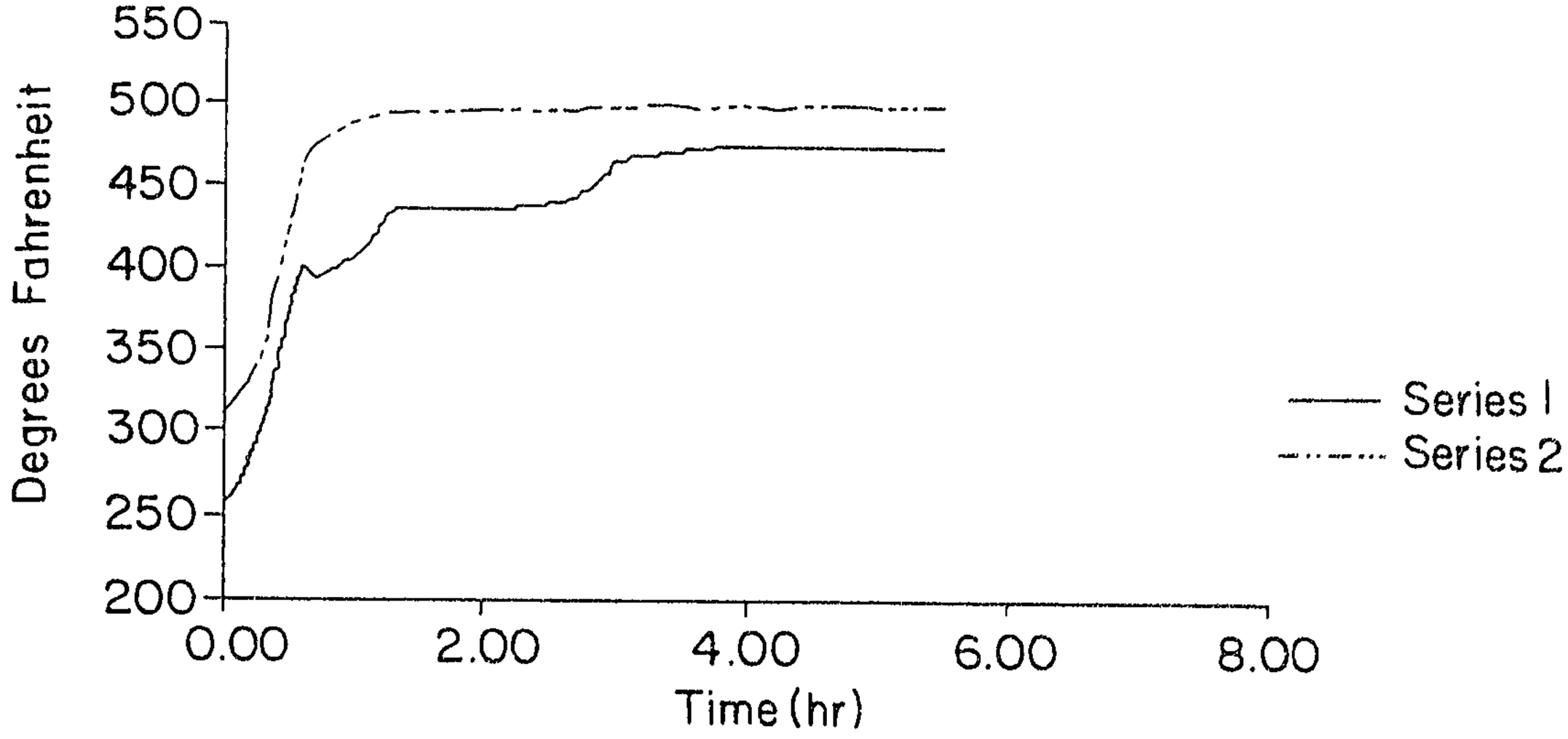
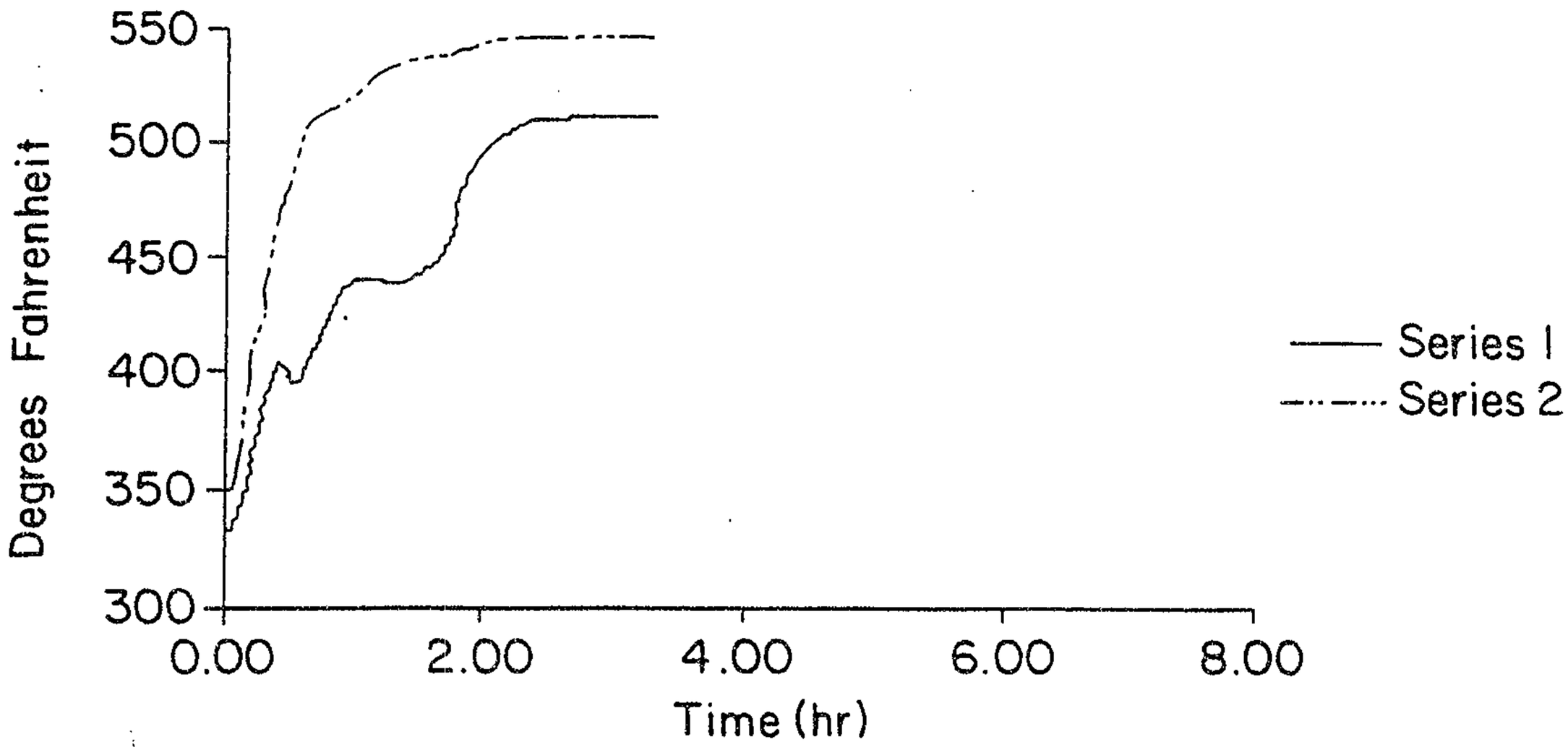

550
500
450
400
350
300
250
200
Degrees Fahrenheit
0.00
2.00
4.00
6.00
8.00
Time (hr)
Series 1
Series 2

FIG. 4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Degrees Fahrenheit
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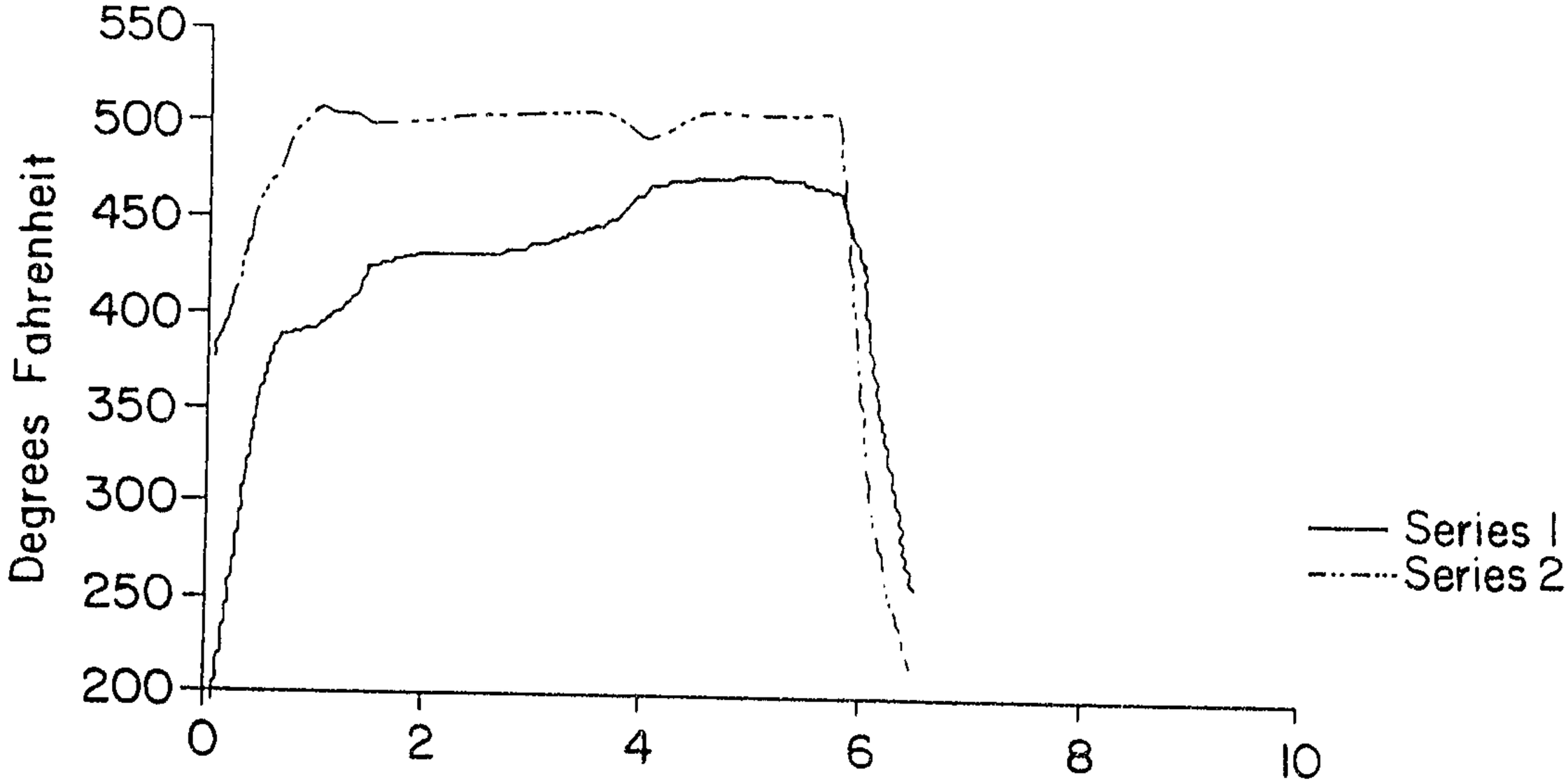
Time (hr)
Series 1
Series 2

FIG. 5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Degrees Fahrenheit
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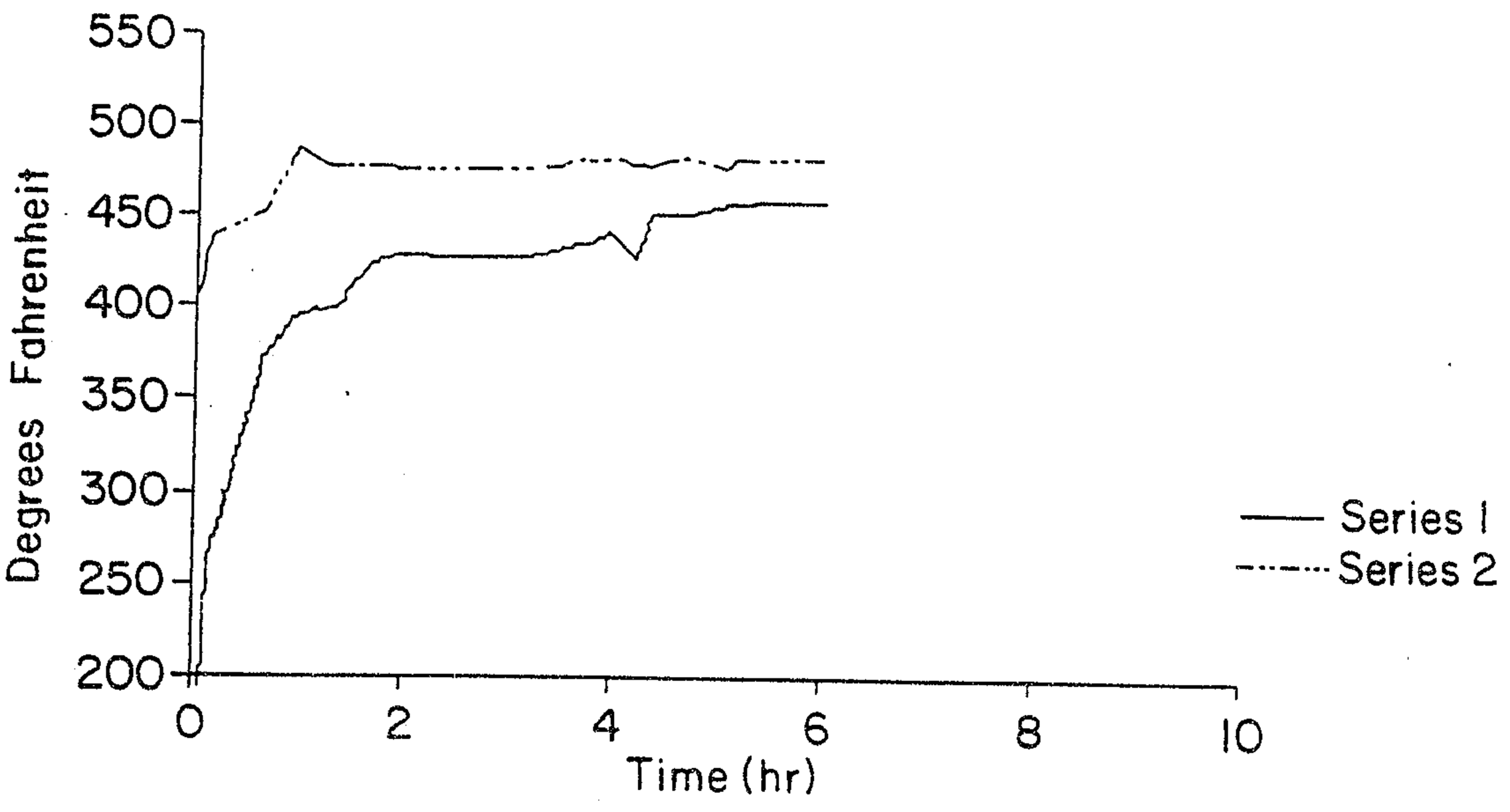
10
Time(hr)
Series 1
Series 2

FIG. 6


550
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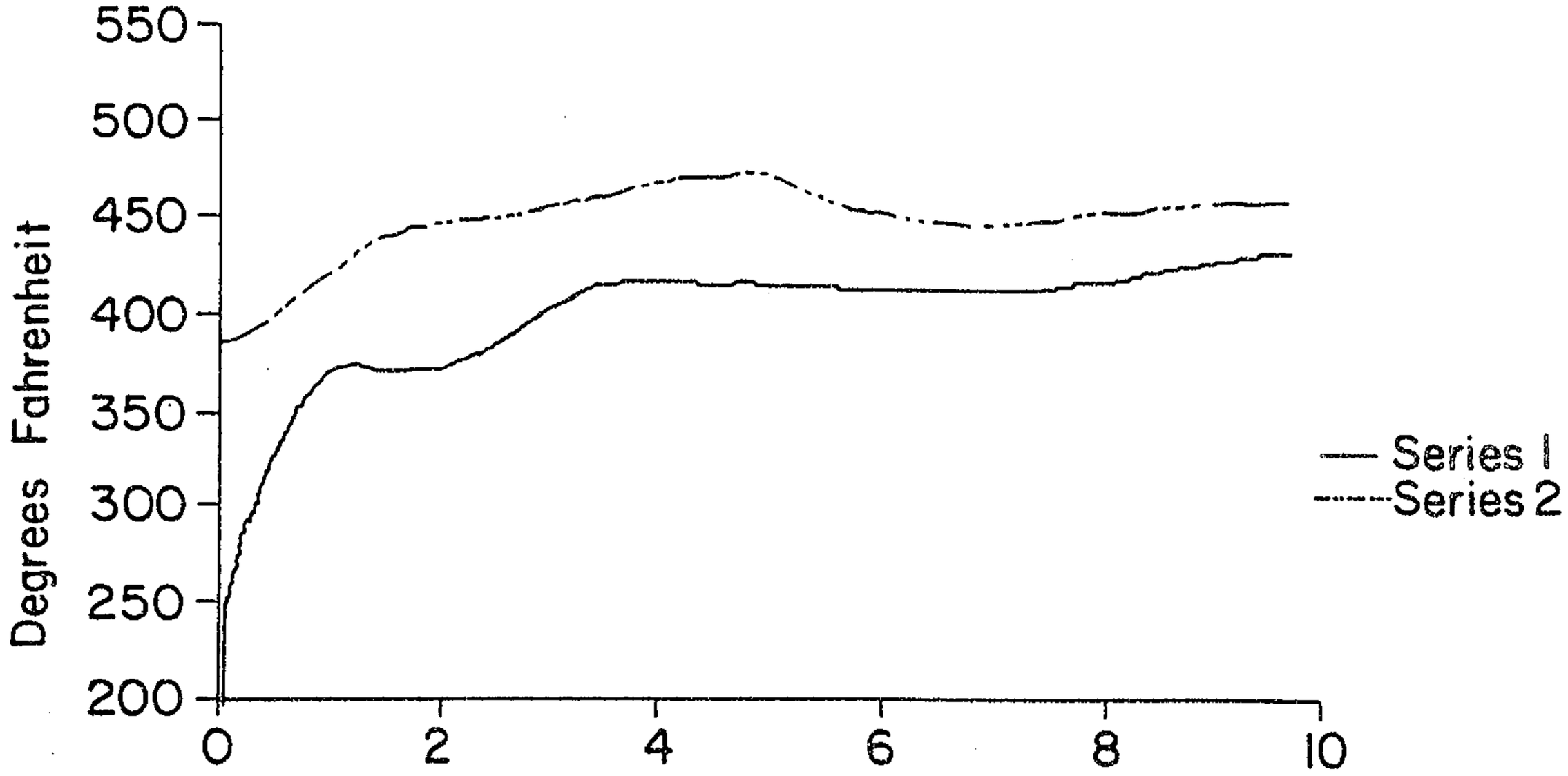
Degrees Fahrenheit
0
2
4
6
8
10
Time (hr)
Series 1
Series 2

FIG. 7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Degrees Fahrenheit
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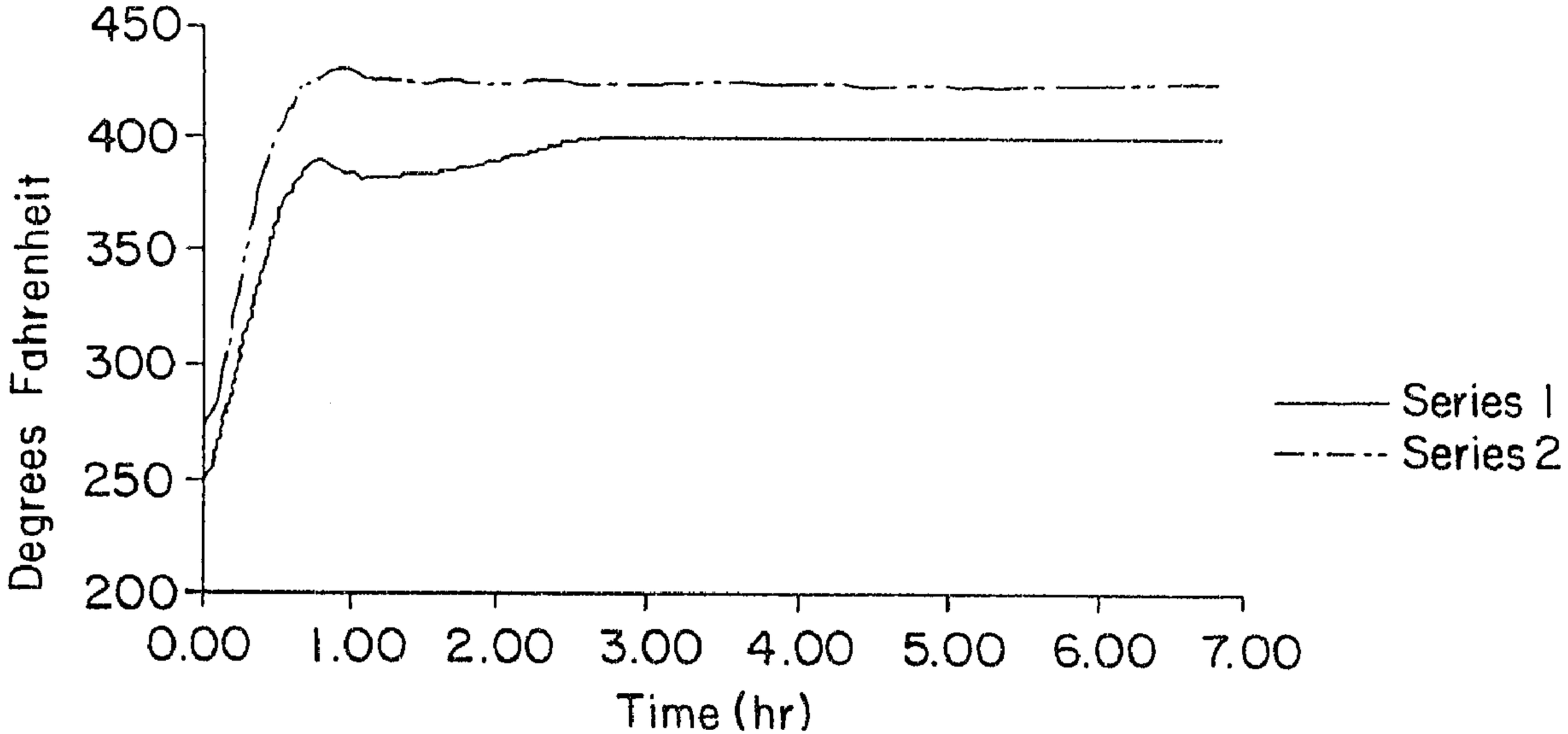
Time(hr)
Series 1
Series 2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250
200
Degrees Fahrenheit
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1.00
2.00
3.00
4.00
5.00
6.00
7.00
Time (hr)
Series 1
Series 2