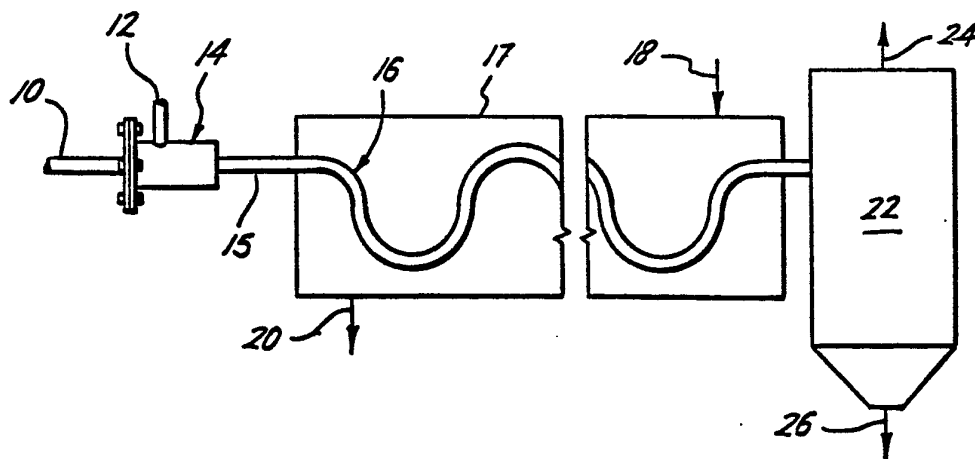




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<p>(21) International Application Number: PCT/US86/00192 (22) International Filing Date: 31 January 1986 (31.01.86)</p> <p>(71) Applicant: THE DOW CHEMICAL COMPANY [US/US]; 2030 Dow Center, Abbott Road, Midland, MI 48640 (US).</p> <p>(72) Inventors: WALKO, Lee, E. ; 103 Pin Oak Street, Lake Jackson, TX 77566 (US). SWANSON, Norman ; 53 Yaupon Court, Lake Jackson, TX 77566 (US). WALLACE, Stephen, B. ; 407 Jasmine Street, Lake Jackson, TX 77566 (US). COOK, Roy, M. ; 1500 Shanks Street, Angleton, TX 77515 (US).</p> <p>(74) Agent: RUSSELL, H., David; The Dow Chemical Company, P.O. Box 1967, Midland, MI 48641-1967 (US).</p>		<p>(81) Designated States: AU, BE (European patent), DE (European patent), FR (European patent), GB (European patent), IT (European patent), JP, KR, NL (European patent), SE (European patent).</p> <p>Published <i>With international search report.</i></p>

(54) Title: PROCESS FOR CONVERTING A THERMOPLASTIC POLYMER INTO SPHEROIDAL AGGLOMERATED GRANULES



(57) Abstract

Thermoplastic polymers in solutions of organic solvents are converted to granules of relatively uniform sizes and a narrow distribution range by passing the polymer solution through a jet nozzle (52) to form a high velocity stream, injecting super heated steam into the high velocity stream to form a suspension of fine polymer particulates in a gas stream, passing the suspension into a uniformly heated serpentine agglomeration tube (16) having a series of at least 6 semi-circular turns (30, 32, 34) wherein the particulates are substantially completely agglomerated into granules and the granules are separated from the gas stream.

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PROCESS FOR CONVERTING A THERMOPLASTIC
POLYMER INTO SPHEROIDAL AGGLOMERATED GRANULES

This invention relates to a process for converting a solution of a thermoplastic polymer in a volatilizable solvent into a plurality of essentially spheroidal agglomerated granules.

5 It is well known in the art that various liquid foodstuffs such as milk, eggs, orange juice, and coffee, etc. can be spray dried by steam or hot air. In U.S. patent 3,039,107, dated 6-12-62, there is disclosed a method wherein these dried food products
10 are agglomerated by contact with a spray of the untreated liquid food.

 It is further known from the following patents that polymeric particulates and/or granules in water slurries can be produced from organic slurries or
15 solutions of various polymers with steam precipitation:

5 U.S. 2,592,814 (4-15-52)
U.S. 3,050,113 (8-21-62)
U.S. 3,202,647 (8-24-65)
U.S. 3,287,301 (11-22-66)
U.S. 3,306,342 (2-28-66)
U.S. 3,427,370 (2-11-69)
U.S. 3,450,184 (6-17-69)
U.S. 3,596,700 (8-3-71)
U.S. 3,862,103 (1-21-75)

10 The following patents show that it is known
to produce dry or substantially dry polymeric granules
from polymer solutions with steam precipitation:

15 U.S. 3,508,339 (4-28-70)
U.S. 3,804,145 (4-16-74)
U.S. 3,968,003 (7-6-76)
U.S. 4,209,912 (7-1-80)
U.S. 4,212,967 (7-15-80)

20 In addition to the foregoing, it is known
from U.S. 4,252,968 (2-24-81) that polycarbonate
powders prepared in U.S. 4,212,967 can be agglomerated
in a stirred and heated tubular drier wherein the
powders are heated to 165-190°C.

25 While the above preparation of polymer
granules in water slurries appears to be effective, it
is a distinct disadvantage to subsequently separate out
the water and remove the residual water absorbed therein.
Furthermore, it is a distinct disadvantage in 4,252,968
to make polymer powders and subsequently agglomerate
these in a rotating mechanical device which has the
30 possibility of mechanical breakdowns.

This invention is directed to a process for converting a thermoplastic polymer in a solution of a volatilizable organic solvent into a plurality of essentially spheroidal agglomerated granules of relatively uniform sizes. The process of this invention comprises:

- (A) passing said solution through a jet nozzle to form a high velocity stream,
- 10 (B) injecting super heated steam into said stream to form a turbulent suspension of fine polymer particulates in a gas stream of vaporized organic solvent and steam,
- 15 (C) passing said suspension into a uniformly heated serpentine agglomeration tube having a uniform diameter and having a series of adjoining circular turns of at least 6 semi-circular turns wherein the residence time of said suspension in said tube is sufficient for substantially complete agglomeration of said particulates, and
- 20 (D) separating the granules from said gas stream.
- 25

Fig. 1 shows the apparatus used in the instant process which includes a steam precipitator 14, an agglomeration tube 16, and a cyclone 22.

30 Fig. 2 shows a modification of the agglomeration tube wherein the serpentine tube of Fig. 1 is modified to include 360° turns.

Fig. 3 shows an isometric view of the tube and shell shown in Fig. 1.

Fig. 4 shows an isometric view of a modified tube and shell showing a series of 180° turns in a vertical plane combined with transverse 360° turns.

Fig. 5 is a cross section view of the steam precipitator taken on line 5-5 of Fig. 6.

Fig. 6 is an end view of the steam precipitator.

In the drawings, the steam precipitator is generally shown at 14. An inlet pipe 10 conveys a polymer solution in an organic solvent to the precipitator 14 where it is contacted with superheated steam from the steam inlet 12. A connector pipe is shown at 15 which is screwed into and joins the steam precipitator 14 and the agglomeration tube 16. The necessary connecting couplers are not shown.

The tube 16 is supported by supports (not shown) in a heating shell 17 which is shown to be rectangular but can be cylindrical if desired. The shell 17 is heated to the proper drying temperature by low process steam which comes in the inlet 18 and is removed by the outlet 20.

The particles which become granules are blown by the steam pressure into a cyclone separator 22 which has an upper outlet 24 for water vapor and organic solvent vapor and a lower outlet 26 for agglomerated granules.

The tube 16 can have various configurations such as upper 360° turns 28 and lower 360° turns 30 as well as upper 180° turns 32 and lower 180° turns 34 and various combinations of these such as a series of 360° turns followed by a series of 180° turns or alternating 180° turns and 360° turns all in one vertical plane as is illustrated in Fig. 2.

In a similar manner, the 180° turns 32 and 34 can be alternated with transverse 360° turns 36 and 37 in a different plane as is illustrated in Fig. 4.

The polymer solution enters the steam precipitator 14 at the threaded inlet 46 and flows through the large internal bore 48 to the restriction 50 where the velocity is greatly increased. The polymer solution flows out of the jet nozzle 52 into the flow of superheated steam which flows from inlet 12 through internal space 54 around the conical bevel 56 and into the polymer solution at a velocity sufficient to disintegrate the solution into stream of fine particles suspended in the superheated steam which exits out of the threaded outlet 60.

The steam precipitator 14 is provided with an inner body 40 which is adjustable with respect to the outer body 38 by means of one or more shims 42. Fastening means such as bolts and nuts 44 are provided to keep the assembly together. By means of the shims 42 a proper spacing between the conical bevel 56 and the conical seat 58 is provided which will give a thin sheet of superheated steam at the proper velocity to break up the stream of polymer into fine particles.

In the process of this invention, a polymer solution in an organic solvent is pumped into a jet nozzle to form a stream having a velocity in the range from about 1 to 100 feet per second (0.3 to 30.5 m/s) and preferably 10 to 50 feet per second (3.0 to 15.2 m/s). While polymer solutions in methylene chloride, ethylene dichloride or monochlorobenzene are preferred, other thermoplastic polymers such as, for example, polyethylene, polystyrene, polybutadiene, and polyisoprene can also be processed when they are dissolved in suitable volatilizable organic solvents.

Superheated steam having a temperature in the range from 100 to 500°C and preferably in the range from 190 to 230°C is then injected in a conical stream into the polymer stream to break up the polymer solution into a fine mist of polymer particles suspended in the steam and vaporized solvent.

The suspension is blown into the agglomeration tube having a series of circular turns wherein the particles are heated by rolling contact with the hot inner walls of the tube so that they become sticky and adhere to each other but not to the walls of the tube due to the velocity of the gas stream through the tube. As the particles pass through the tube they constantly roll over and over due to the plurality of turns and become substantially larger and more or less spherical.

In the preferred form of the agglomeration tube, the tube consists of a serpentine tube having a series of 6 to 20 upper and lower 180° turns in the same plane. While the actual number of turns is not critical, it has been found that in general one must

use at least 6 turns to achieve adequate rounding of the granules and, on the other hand, a number greater than 20 requires a greater gas pressure to push the granules through the tube or pipe turns and can cause
5 partial or complete blockage of the tube. The same design criteria applies to the other more complex configurations.

The exterior walls of the tube are heated by process steam so as to maintain a uniform temperature
10 in the range from 80°C to 170°C and preferably a range from 125°C to 150°C.

In general, the residence time of the particles in the tube is in the range from 0.01 to 60 seconds and preferably in the range from 0.1 to 2
15 seconds. It is to be understood that the residence time is a direct function of several variables such as the feed rates of the superheated steam and/or the polymer solution, the temperature of the superheated steam and the temperature of the process steam used to
20 heat the agglomeration tube. In any event, the residence time is so chosen that the particulates are substantially completely agglomerated into larger sized granules of a random shape which can generally be described as rounded, spheroidal, bead-shaped, etc.
25 Some of the granules are oblate spheroids and some are rather like flat pebbles but the majority appear to be essentially spheroidal. An important feature of this invention is that the granules are of an essentially uniform size range or mesh range with very little dust
30 or powder.

The granules are carried by the gas stream into a conventional cyclone separator wherein the organic solvent vapor and water vapor are taken overhead for recovery of the solvent by condensation. The granules are removed from the bottom and are further processed by mechanical indirect steam dryers to remove residual water and solvent before being processed in a conventional vented extruder and chopper to achieve polycarbonate pellets of suitable purity for molding and/or sale.

The invention is further illustrated by the following examples which are presented to illustrate the invention further:

Example 1

300 lb./hr. (37.8 g/s) of a 10 percent polycarbonate solution at 25°C using methylene chloride as the solvent was fed to a steam precipitator as shown in Fig. 1 of the drawings. 115.5 lb./hr. (14.55 g/s) of 200 psig (1.38 MPa gage) utility steam (200°C) was also applied to the precipitator.

The internal dimensions of the precipitator were 0.312" (7.92 mm) I.D. on the polycarbonate injection barrel and 0.375" (9.52 mm) I.D. on the mixing throat. The steam flow area was adjusted to give a 30 psi (207 kPa) pressure drop across the annulus.

A fine dispersion of minute polycarbonate particulates was formed in the mixer. The particulates were then carried into the agglomeration tube. The particulates were in a tacky state and were recombined into a spherical-like granules. This was done thru

the alternating circular turns in the agglomeration tube. The tube was made of 3/8" (9.525 mm) stainless steel tubing with an I.D. of 0.305" (7.75 mm) and was 7' (2.1 m) in length. The tube contained 20 bends of 180° each similar to Fig. 1 of the drawing wherein each bend had an inside radius of about one inch.

Eighteen lb./hr. (2.27 g/s) of 40 psig (276 kPa gage) utility steam (132°C) was used to control the heat to the shell. The average heat transfer coefficient for the shell was 135 BTU/hr. ft.²-°F (767 w/(m²·k)).

The final polycarbonate granules obtained from the cyclone contained 40% H₂O, by weight and 1.5 percent methylene chloride. The dry bulk density of the polycarbonate granules was 0.2 grams per cubic centimeter. The product distribution was between #4 and #12 mesh (4.75 mm and 1.68 mm) (U.S. Sieve Series) with 86% by weight in the #4 to #8 mesh range (4.75 and 2.38 mm).

20 Examples 2-7

A 10 percent by weight polycarbonate solution in methylene chloride feed solution was fed at various rates in pounds per hour (g/s) to a steam precipitator as shown in Fig. 1 of the drawings using essentially the process parameters of Example 1. The apparatus had an agglomeration tube made from a 0.625 inch (15.875 mm) outside diameter 316 stainless steel tube having a wall thickness of 18 BWG gage or 0.048 inches (1.22 mm). The tube was bent into a series of 15 turns of 180° with an inside radius of 2.625 inches (66.675 mm).

The superheated steam rate was also varied to give a constant polymer solution to steam ratio of 3.95 to 1.

The recovered granules were given a sieve 5 analysis and the results of each example are set forth in Table I.

TABLE I

<u>Example</u>	<u>Polymer Feed Rate</u>		<u>U.S. Sieve Analysis</u> <u>(% of Total wt.)</u>				
	<u>lbs./hr</u>	<u>(g/s)</u>	<u>>3</u> <u>(>6.73 mm)</u>	<u>>4</u> <u>(> 4.75 mm)</u>	<u>>8</u> <u>(>2.38 mm)</u>	<u><8</u> <u>(<2.38 mm)</u>	
2	1040	(131.0)	28.8	56.2	14.5	0.5	
3	1000	(126.0)	29.6	55.6	14.6	0.2	
4	950	(119.7)	22.7	55.4	21.9	0.1	
5	900	(113.4)	20.1	53.7	25.7	0.4	
6	875	(110.2)	20.4	53.3	25.9	0.4	
7	850	(107.1)	17.6	46.4	35.6	0.3	

The above data indicates that the process of this invention produces a mixture of various size granules wherein a substantial majority of the granules are greater than U.S. Sieve #4 (0.187 inches or 4.76 mm) and very few of the granules are less than U.S. Sieve #8 (0.0937 inches or 2.38 mm).

1. A process for converting a thermoplastic polymer in a solution of a volatilizable organic solvent into a plurality of essentially spheroidal agglomerated granules of relatively uniform sizes which comprises
- 5 (A) passing said solution through a jet nozzle to form a high velocity stream,
- (B) injecting super heated steam into said stream to form a turbulent suspension of fine polymer particulates in a gas
- 10 stream of vaporized organic solvent and steam,
- (C) passing said suspension into a uniformly heated serpentine agglomeration tube having a uniform diameter and having a
- 15 series of at least 6 semi-circular turns wherein the residence time of said suspension in said tube is sufficient for substantially complete agglomeration of said particulates, and
- 20 (D) separating the granules from said gas stream.
2. The process of Claim 1 wherein said superheated steam has a temperature in the range from 100° to 500°C, said heated tube has a temperature in
- 25 the range from 80° to 170°C, and said residence time is in the range from 0.01 to 60 seconds.

3. The process of Claim 2 wherein said superheated steam has a temperature in the range from 190° to 230°C, said heated tube has a temperature in the range from 125° to 150°C, and said residence time
5 is in the range from 0.1 to 2 seconds.

4. The process of any of Claims 1, 2, or 3 wherein the thermoplastic polymer is a polycarbonate polymer.

Fig. 1

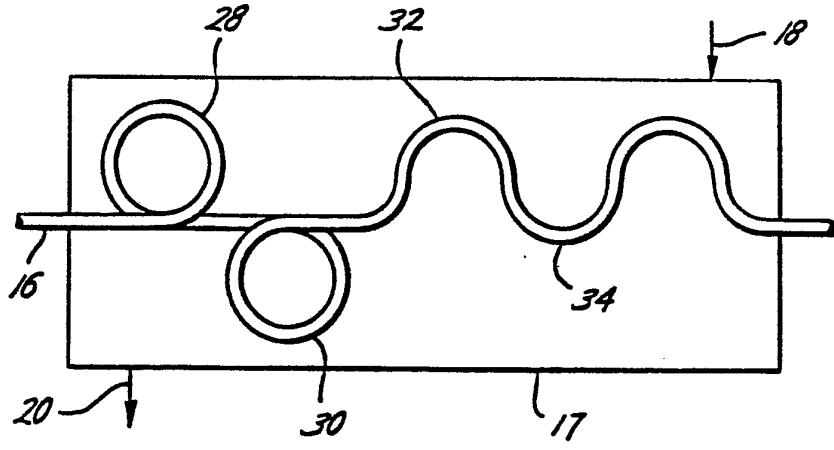
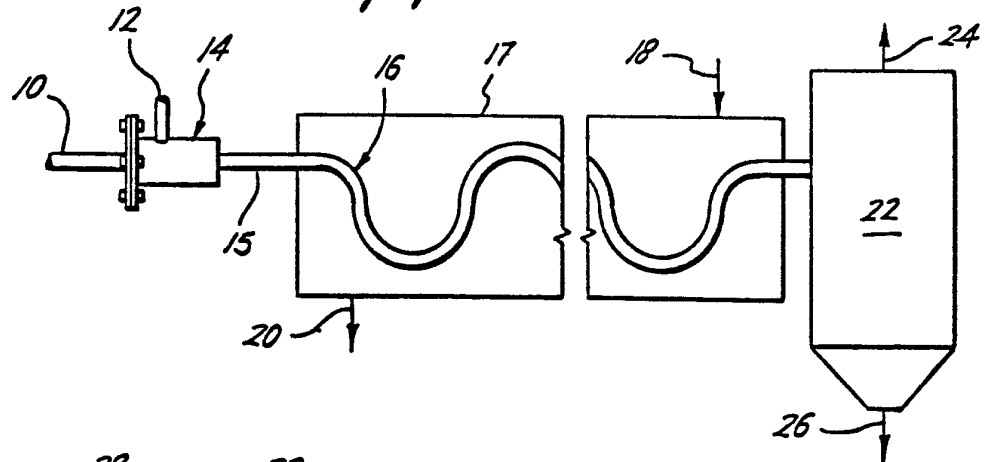


Fig. 2

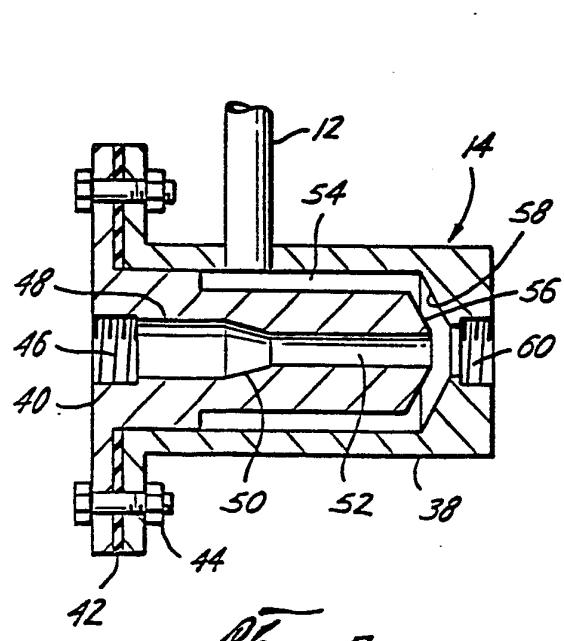


Fig. 5

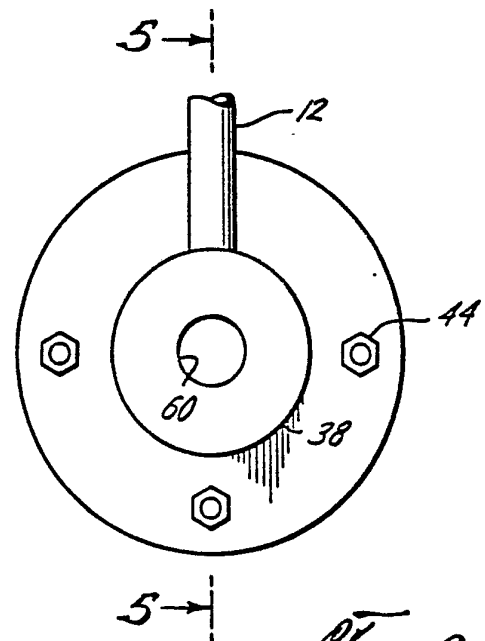
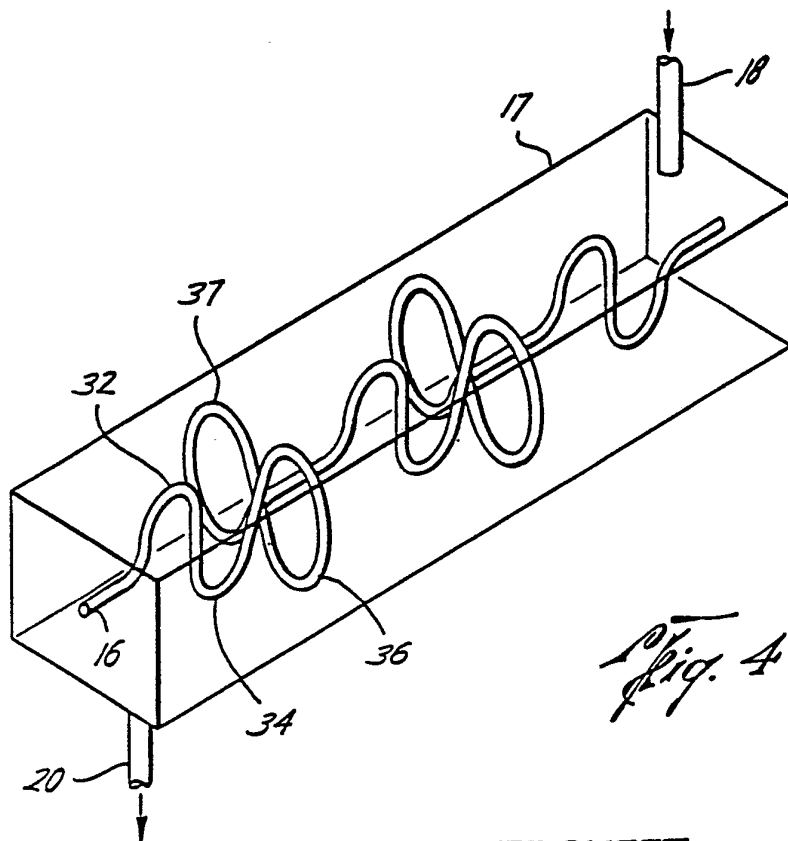
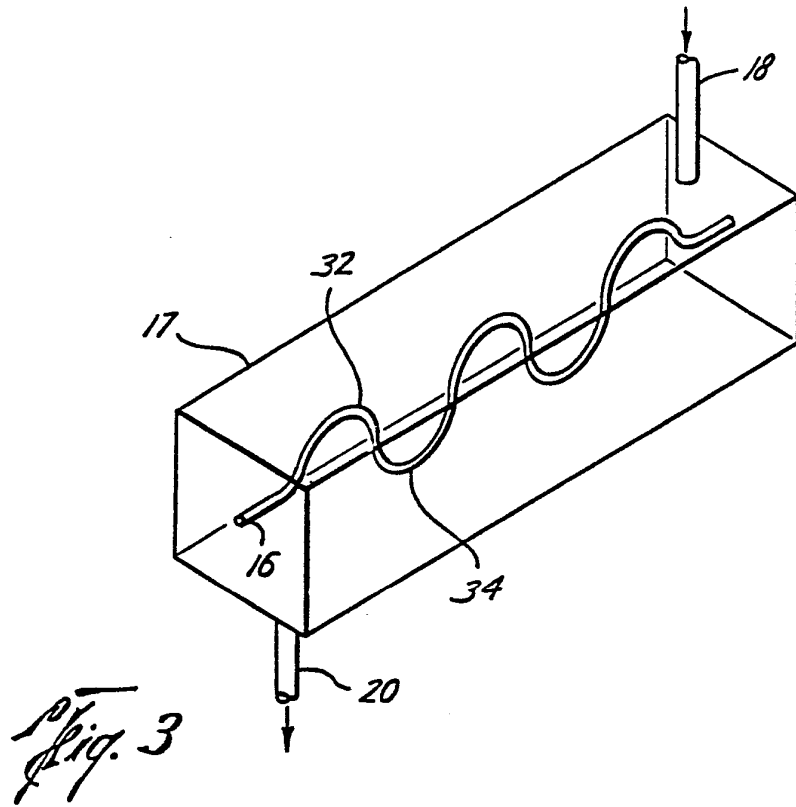


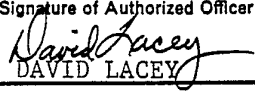
Fig. 6



SUBSTITUTE SHEET

INTERNATIONAL SEARCH REPORT

International Application No PCT/US86/00192

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		
INT. CL.4 B01D 1/18		
US. CL. 159/44, 48.1, DIG.10; 23/313R; 264/12, 15, 117, 121		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁴		
Classification System	Classification Symbols	
U.S.	264/3, 12, 15, 117, 121, 176F, 611, 629; 159/4.4. 47, 48.1 16.3, DIG. 10; 23/312, 313R; 528/500,503	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁵		
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
A	US,A, 3,508,339, PUBLISHED 28 APRIL 1970, NEBLETT ET AL.	1-4
A	US,A, 4,212,967, PUBLISHED 15 JULY 1980, GOVONI ET AL.	1-4
<p>* Special categories of cited documents: ¹⁵</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"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)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"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</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"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.</p> <p>"&" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search ²		Date of Mailing of this International Search Report ²
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