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2 PREPARATION OF MAGNESIUM-FLUOROPOLYMER
3 PYROTECHNIC MATERIAL4
5 by6 George W. Naufflett
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8 Lalit Chordia

9 BACKGROUND

10 This invention relates to energetic materials and more particularly to methods of
11 producing energetic materials from metals and fluoropolymers.12 Pyrotechnics are mixtures of substances that produce noise, light, heat, smoke, or motion
13 when ignited. They are used in matches, incendiaries, and other igniters; in fireworks and flares;
14 in fuses and other initiators for primary explosives; in delay trains; and for powering mechanical
15 devices. Military pyrotechnics include a wide range of devices for illumination, signaling,
16 incineration, and gas generation. Military pyrotechnic devices are characterized by more rugged
17 construction and greater resistance to adverse environmental conditions with concomitant higher
18 cost, reliability, and safety than are civilian pyrotechnics.19
20 Magnesium/Teflon/Viton (MTV) pyrotechnics are used by the Armed Forces to
21 manufacture rocket motor igniters and flare decoys. MTV is currently manufactured using the
22 shock-gel process in which: (1) the Viton binder is dissolved in acetone; (2) the magnesium and
23 Teflon particles are added to the Viton/acetone solution to form a slurry; (3) and hexane is added
24 to the slurry to shock the slurry and precipitate the Viton out of solution onto the surfaces of the
25 magnesium and Teflon particles. The solvent is then decanted from the mixture and the
26 procedure is repeated to ensure that all the remaining acetone is washed from the pyrotechnic
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1 material. Although the process is extremely effective in coating the magnesium and Teflon, it is a
2 lengthy batch process which requires an extremely large quantity of solvent (acetone and hexane)
3 to coat the magnesium and Teflon with the Viton binder. It takes five 55-gallon drums of solvent
4 to process 200 pounds of MTV. The collected acetone and hexane mixture must be disposed of
5 as hazardous waste due to the toxic nature of the solvent.
6

7 It would be desirable to provide an method of producing high quality energetic materials
8 composed of a mixture of magnesium (or magnesium alloys, aluminum, aluminum alloys, etc.)
9 particles and polytetrafluoroethylene (e.g., Teflon) particles in a vinylidene fluoride-
10 hexafluoropropylene copolymer (e.g., Viton A, Fluorel) binder without generating large volumes
11 of hazardous waste.
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13 SUMMARY

14 Accordingly, an object of this invention is to provide a new process for producing
15 magnesium/fluoropolymer energetic materials.

16 Another object of this invention is to provide a process for producing
17 magnesium/fluoropolymer energetic materials without producing large volumes of hazardous
18 waste.

19 These and other objects of this invention are accomplished by providing a process
20 comprising:
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22 (1) dissolving a vinylidene fluoride-hexafluoropropylene copolymer in a ketone solvent
23 that is acetone, methyl ethyl ketone, or mixtures thereof;

24 (2) forming a paste by adding a mixture of polytetrafluoroethylene particles and reactive
25 metal particles that are magnesium particles, magnesium alloy particles, aluminum particles,
26 aluminum alloy particles, or mixtures thereof to the solution form in step (1);
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1 (3) adding liquid CO₂ to the paste formed in step (2) to cause the vinylidene fluoride-
2 hexafluoropropylene copolymer to precipitate out of the ketone solvent and coat the
3 polytetrafluoroethylene particles and the reactive metal particles while the paste is agitated; and

4 (4) separating the vinylidene fluoride-hexafluoropropylene copolymer-coated
5 polytetrafluoroethylene particles and reactive metal particles from the ketone solvent and the
6 CO₂.
7

8 The ketone solvent and the CO₂ are preferably separated from each other and reused.

9 BRIEF DESCRIPTION OF THE DRAWINGS

10 A more complete understanding of the invention and many of its attendant advantages
11 thereof will be readily appreciated as the same becomes better understood by reference to the
12 following detailed description when considered in connection with the accompanying drawings,
13 wherein:
14

15 FIG. 1 is a flow diagram illustrating the process of this invention; and

16 FIG. 2 is a general schematic drawing of equipment which may be used in the process of
17 this invention.

18 DESCRIPTION

19 The process of the present invention produces energetic materials by coating a mixture of
20 polytetrafluoroethylene (Teflon) particles and reactive metal particles with a copolymer
21 hexafluoropropylene and vinylidene fluoride. The reactive metal particles are preferably
22 magnesium particles, magnesium alloy particles, aluminum particles, aluminum alloy particles, or
23 mixtures of these particles, with the magnesium particles being the most preferred. The
24 vinylidene fluoride-hexafluoropropylene copolymers which may be used in this process are
25 soluble in acetone or methyl ethyl ketone and insoluble in carbon dioxide (CO₂). The
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[REDACTED]

[REDACTED]

[REDACTED]

[REDACTED]

[REDACTED]

[REDACTED]

[REDACTED]

[REDACTED]

[REDACTED]

1 hexafluoropropylene(70:30) copolymer (Viton or Fluorel) are mixed together to produce a
2 solution of the copolymer in acetone. The solution will preferably comprise from about 9 to
3 about 25 and more preferably from 16 to 19 weight percent of the vinylidene fluoride-
4 hexafluoropropylene copolymer with the remainder of the solution being acetone.

5
6 As shown in Fig.1, the next step is to mix magnesium particles and
7 polytetrafluoroethylene particles with the vinylidene fluoride-hexafluoropropylene(70:30)
8 copolymer /acetone solution to produce a slurry. The slurry is a paste having a consistency
9 similar to poured concrete. The amounts of magnesium, polytetrafluoroethylene, and vinylidene
10 fluoride-hexafluoropropylene(70:30) copolymer added are the amounts required to produce the
11 desired energetic composite. For instance, in the examples, 54 weight percent of magnesium
12 particles, 30 weight percent of polytetrafluoroethylene (Teflon), and 16 weight percent of
13 vinylidene fluoride-hexafluoropropylene (70:30) copolymer (Viton or Fluorel) were used to
14 prepare a MTV pyrotechnic material.
15

16 Referring again to the flow chart of Fig.1, the next step is the shock or super-shock step in
17 which the vinylidene fluoride-hexafluoropropylene(70:30) copolymer is shocked or driven from
18 the acetone to precipitate as a coating on the polytetrafluoroethylene particles and the magnesium
19 particles. It is critical that the slurry is vigorously agitated (e.g., stirred) during this shock step in
20 order to produce a high quality product. This shock precipitation step is run in a pressure vessel
21 in which the outlet valve is closed and only the supercritical CO₂ inlet is open. In the presence of
22 acetone, the critical temperature of CO₂ is raised from 30.1°C to about 120°C. As a result, the
23 supercritical CO₂ is converted to liquid CO₂ in the pressure vessel. Because CO₂ and acetone are
24 infinitely soluble in each other, the CO₂ readily dissolves in the acetone to produce a CO₂/acetone
25 solution. The vinylidene fluoride-hexafluoropropylene(70:30) copolymer is soluble in acetone
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1 but insoluble in CO₂. As a result, the CO₂ shocks or drives the copolymer out of the acetone as a
2 precipitate that coats the polytetrafluoroethylene particles and the magnesium particles. Because
3 the acetone is recycled in the preferred embodiment of this invention, it is critical that enough
4 CO₂ is added to drive all of the vinylidene fluoride-hexafluoropropylene(70:30) copolymer from
5 the acetone. Even a small amount of the copolymer will accumulate in the system and clog
6 valves and sensors, making the system dangerous to operate. At 40 weight percent acetone (60
7 weight percent CO₂) the recovered acetone contained no vinylidene fluoride-
8 hexafluoropropylene(70:30) copolymer (Fluorel). However, at 80 weight percent acetone (20
9 weight percent CO₂) the recovered acetone contained 36.4 weight percent Fluorel and at 54
10 weight percent acetone (46 weight percent CO₂) the recovered acetone contained 3 weight percent
11 Fluorel. Therefore, CO₂ is preferably added until the acetone/CO₂ solution contains at least 60
12 weight percent of CO₂ and no more than 40 weight percent acetone.
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15 After all the vinylidene fluoride-hexafluoropropylene(70:30) copolymer has been
16 precipitated from the acetone, the acetone is removed in an extraction step (see Fig. 1). This is
17 done by opening the outlet valve in the pressure vessel and continuing the input of the
18 supercritical CO₂ while the slurry is vigorously agitated (e.g., stirred). After the acetone/CO₂
19 solution has been flushed out of the reactor, the critical temperature of the CO₂ drops back down
20 to about 30.1C and the supercritical CO₂ is no longer liquefied. The input of supercritical CO₂ is
21 continued while solid MTV product is vigorously agitated until all the acetone adhering to the
22 MTV particles is removed. After no more acetone is detected in the supercritical CO₂ exhaust
23 leaving the pressure vessel, the supercritical CO₂ input is stopped and the solid MTV product is
24 collected. The free-flowing solid MTV crumb product may then be extruded using conventional
25 means.
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1 In the preferred embodiment as indicated in Fig. 1, the CO₂ and acetone flushed from the
2 pressure vessel are separated and then recycled. In the examples, a Cyclone separator is used to
3 separate the acetone as a liquid and the CO₂ as a gas.

4 In the general process of this invention the carbon dioxide (CO₂) which is fed into the
5 pressure vessel in the shock step and the extraction step (acetone or methyl ethyl ketone removal)
6 is preferably at a pressure of from about 1,000 to about 10,000, more preferably from 1,000 to
7 5,000, and still more preferably from 2,000 to 4,500 psi, and at a temperature or preferably from
8 about 15 to about 80, more preferably from 31 to about 80, and still more preferably from 60 to
9 80°C. The CO₂ will be either in the form of a liquid or a supercritical fluid. If the CO₂ is both at
10 a temperature above its critical temperature (30.1C) and at a pressure about its critical pressure
11 (1044 psi?), the CO₂ feed will be a supercritical fluid. However, in the presence of either acetone
12 or methyl ethyl ketone the critical temperature of CO₂ is raised well above 80°C and the
13 supercritical CO₂ fluid is converted into liquid CO₂.

14 The CO₂ readily dissolves in the acetone or methyl ethyl ketone. The vinylidene fluoride-
15 polyhexafluoropropylene copolymers are soluble in acetone or methyl ethyl ketone but insoluble
16 in CO₂. Thus, the CO₂ shocks or drives the copolymer from the ketone solution and the
17 precipitating copolymer forms a coating on the polytetrafluoroethylene particles and the reactive
18 metal particles. Because the acetone or methyl ethyl ketone is recycled, it is critical that all
19 vinylidene fluoride-hexafluoropropylene copolymer is removed (precipitated) from the
20 ketone/CO₂ solution. As a result CO₂ should be added until the ketone (acetone, methyl ethyl
21 ketone, or mixtures thereof)/CO₂ solution preferably contains at least 60, more preferably at least
22 70, still more preferably at least 80, and most preferably at least 90 weight percent of CO₂. The
23 composition of the ketone/CO₂ solution is easily calculated from the weight of ketone (acetone,
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1 methyl ethyl ketone, or mixtures thereof) used and the pressure, temperature, flow rate, and time
2 of flow of the CO₂ feed stream.

3 Fig. 2 shows a schematic drawing of a typical apparatus set up which may be used in the
4 present process where the CO₂ and the acetone are recycled. Shown is a premix vessel 20 in
5 which a MTV premix 22 of magnesium particles and polytetrafluoroethylene (Teflon) particles
6 in a solution of vinylidene fluoride-hexafluoropropylene(70:30) copolymer in acetone is prepared.
7 The MTV premix 22 is mixed by premix agitator blades 30 which are attached to premix agitator
8 shaft 28 which is driven by premix agitator motor 26. After the MTV premix 22 is prepared, the
9 premix valve 34 is opened and the MTV premix 22 is transfer through tube 36 into pressure
10 vessel 54 where the premix is now referred to as MTV material 62. The MTV material 62 starts
11 off as the MTV premix; is converted by the CO₂ shock process step to raw, acetone-containing
12 MTV product; and is finally converted to the dry, acetone-free, free-flowing MTV crumb final
13 product. The MTV material 62 in pressure vessel 54 is agitated by agitator blades 64 which are
14 attached to the pressure vessel agitator shaft 60 which is driven by the pressure vessel agitator
15 motor 58. CO₂ is fed from line 38 into a compressor 40 where the CO₂ is compressed to a
16 pressure of from 1,000 to 5,000 psi and then flows through a hot water heat exchanger 44 which
17 heats the CO₂ above the supercritical temperature. (Hot water flows in through inlet 46, through
18 the heat exchanger 44, and then out through the outlet 48.) The now supercritical CO₂ 50 flows
19 through inlet valve 52 into the reaction vessel 54. Note that premix valve 34 and pressure
20 reduction valve 76 are closed thus sealing the pressure vessel 54. The temperature of the pressure
21 vessel 54 is kept at the temperature of the incoming supercritical CO₂ by a hot water jacket 66
22 which surrounds the pressure vessel 54. Hot water flows in through inlet 68, through the jacket
23 66, and out through the outlet 70. In the presence of acetone, the critical temperature of CO₂ is
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1 greatly raised, causing the supercritical CO₂ to liquefy and be dissolved in the acetone in the
2 MTV material 62. After sufficient CO₂ has been added to shock or precipitate all the vinylidene
3 fluoride-hexafluoropropylene copolymer from the acetone, the pressure reduction valve 76 is
4 opened. Acetone and CO₂ are exhausted through the exhaust line 72 as the agitator blades 64
5 continue to mix the MTV material 62 and supercritical CO₂ 50 continues to flow in through the
6 inlet valve 52. After the bulk of the liquid acetone has been removed from the MTV material 62,
7 the critical temperature of CO₂ is reduced and the supercritical CO₂ is no longer liquefied. The
8 agitation of the now dry MTV material 62 is continued and the flow of supercritical CO₂ is
9 continued until acetone is no longer detected in the exhaust supercritical CO₂. The acetone and
10 CO₂ is removed from the pressure vessel 54 through the exhaust line 72 which feeds the pressure
11 reduction valve 76. From the pressure reduction valve 76 the CO₂ flows (at reduced pressure)
12 through total hydrocarbon detector 80 (which monitors the CO₂ for acetone) and on to a Cyclone
13 separator 82.. The Cyclone separator 82 separates the acetone as a liquid and the CO₂ as a gas.
14 The liquid acetone is drained from the separator 82 through a cyclone separator valve 84 into the
15 recovered acetone line 86. The acetone is recycled for use in a future batch. The CO₂ is passed
16 through line 90 to a CO₂ purifier 92. A line 94 feeds the purified CO₂ to the compressor 40 for
17 reuse in the processes. Additional CO₂ may be added through line 38 as needed. Finally, after all
18 the acetone has been removed from the dry MTV material product 62, the agitator (58,60,64) is
19 turned off and the flow of supercritical CO₂ through inlet valve 52 is stopped. The dry MTV
20 material product 62 is then collected.

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24 The general nature of the invention having been set forth, the following examples are
25 presented as specific illustrations thereof. It will be understood that the invention is not limited to
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1 these specific examples but is susceptible to various modifications that will be recognized by one
2 of ordinary skill in the art.

3 Experimental Super-Shock Process MTV Process

4 MTV paste was prepared in two steps. First the acetone solution of fluorel-2175 or Viton-
5 A was prepared by standing overnight in a stainless steel beaker. Secondly, the magnesium (Type
6 II) and Teflon 7C were slurried into the solution. The paste was added to a 500-mL pressure
7 vessel equipped with a thermocouple, agitator and tachometer. An upward flow of carbon
8 dioxide at 60°C at 136 atm (2,000 psi) quenched the mixture under agitation (400 ± 50 RPM).
9 The MTV crumb was continuously extracted with a flow of supercritical CO₂ until acetone
10 stopped collecting in traps. Dry free flowing gray MTV was poured out of the vessel and about
11 10 to 15% of MTV stuck to the agitator and vessel.
12

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14 Shown in Table 1 is a summary of the MTV batches prepared. The Viton-A was replaced
15 with Fluorel-2175 which has the same CAS number and is used as a direct replacement in MTV
16 production.

17 Efficient agitation was found to be essential for the preparation of free flowing crumb
18 similar to that produced by the Shock-Gel process. MTV Batches using one impeller produced
19 free flowing crumb in 50 gram batches but not at the 100 gram level. The need for efficient
20 agitation was demonstrated when four impeller blades were used. All the 100 to 200 grams
21 batches of MTV crumb produced using four impeller blades were free flowing.
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23 A parameter study was performed to determine the effects of acetone content on MTV the
24 Super-Shock process. The amount of carbon dioxide needed to extract the acetone from the MTV
25 was also investigated. The concentration of acetone at the start of each batch was calculated. At
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1 40% acetone (60% CO₂) the recovered acetone contained no Fluorel. At 80% acetone (20% CO₂)
2 the recovered acetone contained 36.4% Fluorel.

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Table 1

SCF-MTV BATCHES

Acetone extraction 2,000 psi and 60°C

Example	Batch size (g)	Acetone in paste wt %	Acetone in CO ₂ at start wt %	CO ₂ flow	CO ₂ used (g)	Acetone collected wt %	CO ₂ flow (L/min)	Yield %	Fluorel in MTV wt %	Fluorel in acetone wt %	Footnote
1	5	56	16	Down	-	65	-	-	-	-	1
2	5	61	26	Up	-	45	-	-	-	-	2
3	5	61	26	Up	-	46	-	46	-	-	-
4	10	58	56	Up	-	47	-	-	-	-	3
5	5	61	26	Up	-	61	-	-	-	-	-
6	50	40	13	Up	962	33	-	-	-	-	4
7	75	39	21	Up	1216	47	7	-	-	-	5
8	50	44	17	Up	1825	40	10	84	16	0	6
9	50	32	10	Up	897	25	20	86	17	0	7
10	50	41	12	Up	1322	68	5	-	-	-	8
11	100	50	41	Up	800+	-	10	-	-	-	9
12	150	54	68	Up	3015	45	15	-	-	-	-
13	200	-	0	Up	3053	51	15	96	-	-	10
14	200	41	60	Up	3830	23	30	96	12	>0.1	11
15	200	51.6	83	Up	2583	22	15	95	11.9	36.4	12
16	100	52	45	Up	1852	42	15	94	11	2	13
17	100	40	21	Up	1794	53	14	83	14 to 16	>0.1	14
18	175	40	41	Up	1367	41	15	92	16	>0.1	15

¹Jerguson Gauge inert run (Mg replaced with Alumina) - downward flow CO₂ - 3% of Viton collected in trap.²MTV not free flowing - need agitation - Teflon needs to be delumped.³10% extra Viton used - Upward flow CO₂ as Viton/acetone added from top

15 cm/min not fluidized - difficult to remove batch from Jerguson Gauge

- ⁴500-mL pressure vessel, Newport compressor, air controlled back pressure regulator - (Mg replaced with Alumina) - No Viton in collected acetone - inline filter became plugged. Last 300 psi of pressure released from bottom.
- ⁵inert run (Mg replaced with Alumina) - Exit filter became loose. (in future batches connected with fittings).
- ⁶Fluorel (lot FC2175), manganese Type II (lot 92-M-066B), Teflon 7c (lot 970209) extra acetone used to transfer MTV/acetone mix into the vessel - MTV stuck to vessel walls (14%) 0.63 g/mL bulk density - white spots in MTV -Teflon will be delump in blender in next batches - Sensitivity test: Impact 350 mm(NPP3+), 228 mm Brucection; Sliding friction 135 psi; Electrostatic discharge 8.33 Joules - No Viton in collected acetone -
- ⁷THAR Pump used - Teflon delumped in blender 40 sec medium speed - no white pieces in MTV - No Fluorel in collected acetone
- ⁸No Agitation - MTV solid soft cylinder - No white spots uniform gray
- ⁹45% of MTV near agitator was good crumb. The rest of the MTV was a solid piece. - Need multiple agitators - leak in collection system
- ¹⁰Fluorel/acetone (20%) pumped 7 mL/min into pressure vessel at 2000 psi and 50°C - MTV at top 55% Fluorel and 3% Fluorel at bottom - No Fluorel in collected acetone
- ¹¹No smell of acetone - No Viton in collected acetone -Sensitivity test: Impact >1000 mm(NPP3+), >1000 mm Brucection; ABL friction 180 psi; Electrostatic discharge 8.33 Joules - Analysis: Fluorel 11.9%; Mg 56.0%; Teflon 32.1%
- ¹²36.4% Fluorel collected in recovered acetone! In 500 mL vessel 107 mL MTV, 267 mL acetone and 37 mL agitator. This leaves 89 mL for the CO₂
- ¹³2% Fluorel collected in recovered acetone.
- ¹⁴Less than 0.1% of the Fluorel collected in recovered acetone. Part of batch stuck to vessel walls and agitators.
- ¹⁵Less than 0.1% of the Fluorel collected in recovered acetone. Batch 300 atm (4,410 psi) and 60°C

1 Obviously, other modifications and variations of the present invention may be possible in
2 light of the foregoing teachings. It is therefore to be understood that

3 the invention may be practiced otherwise than as specifically described.
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2 PREPARATION OF MAGNESIUM-FLUOROPOLYMER
3 PYROTECHNIC MATERIAL

4
5 ABSTRACT

6 A process for preparing energetic materials by (1) dissolving a vinylidene fluoride-
7 hexafluoropropylene copolymer in a ketone that is acetone, methyl ethyl ketone, or mixtures
8 thereof, (2) adding polytetrafluoroethylene particles and reactive metal (magnesium, aluminum,
9 or their alloys) particles to form a slurry, (3) adding CO₂ to the slurry to precipitate out the
10 copolymer which then coats the polytetrafluoroethylene and reactive metal particles, and (4)
11 separating the copolymer-coated particles from the ketone and CO₂.
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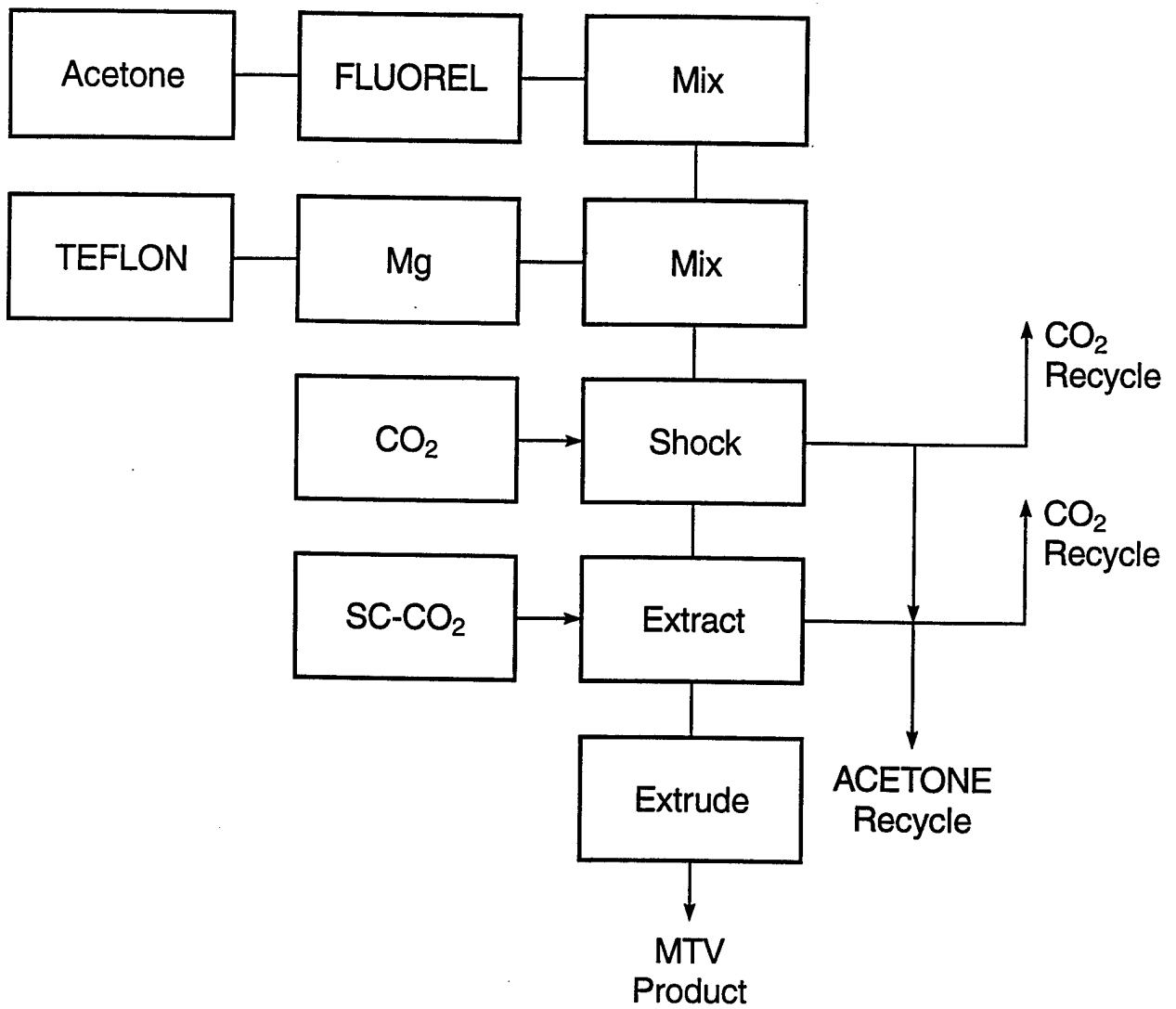


FIG. 1

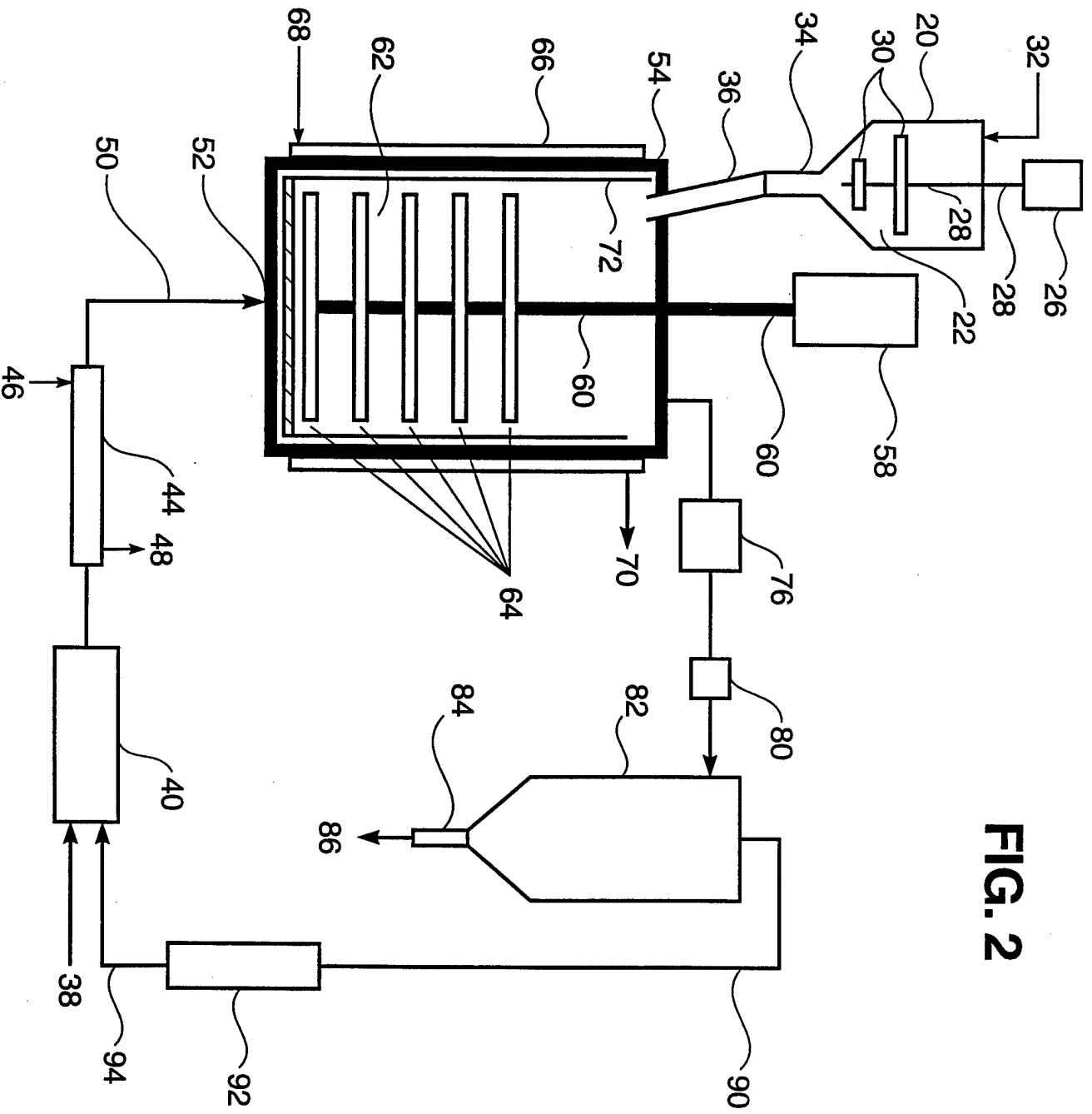


FIG. 2