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Hohmann et al.

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[54] **AUTOMATED PROPELLANT BLENDING**

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[22] Filed: **Aug. 20, 1997**

[51] Int. Cl.⁶ **B01F 15/02**

[52] U.S. Cl. **366/151.1; 422/163; 366/150.1; 366/241; 366/279; 137/93**

[58] Field of Search 366/151.1, 150.1, 366/152.1, 132, 168.1, 241, 279; 137/93; 422/163, 224, 225, 135, 67, 62

[57] **ABSTRACT**

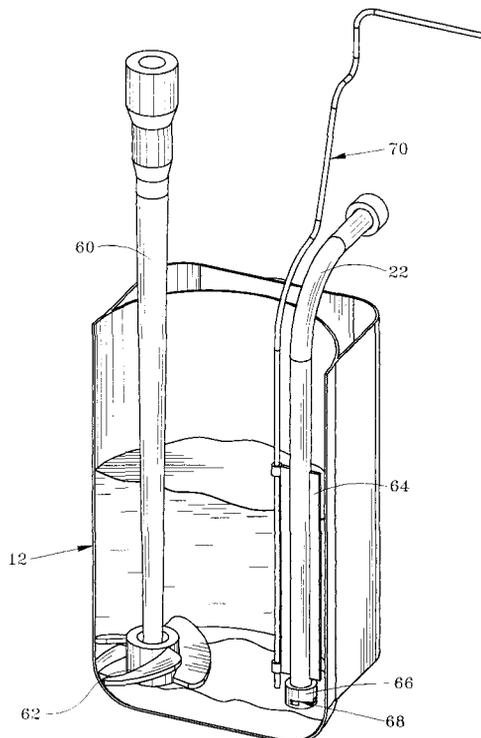
An automated propellant blending apparatus and method uses closely metered addition of countersolvent to a binder solution with propellant particles dispersed therein to precisely control binder precipitation and particle aggregation. A profile of binder precipitation versus countersolvent-solvent ratio is established empirically and used in a computer algorithm to establish countersolvent addition parameters near the cloud point for controlling the transition of properties of the binder during agglomeration and finishing of the propellant composition particles. The system is remotely operated by computer for safety, reliability and improved product properties, and also increases product output.

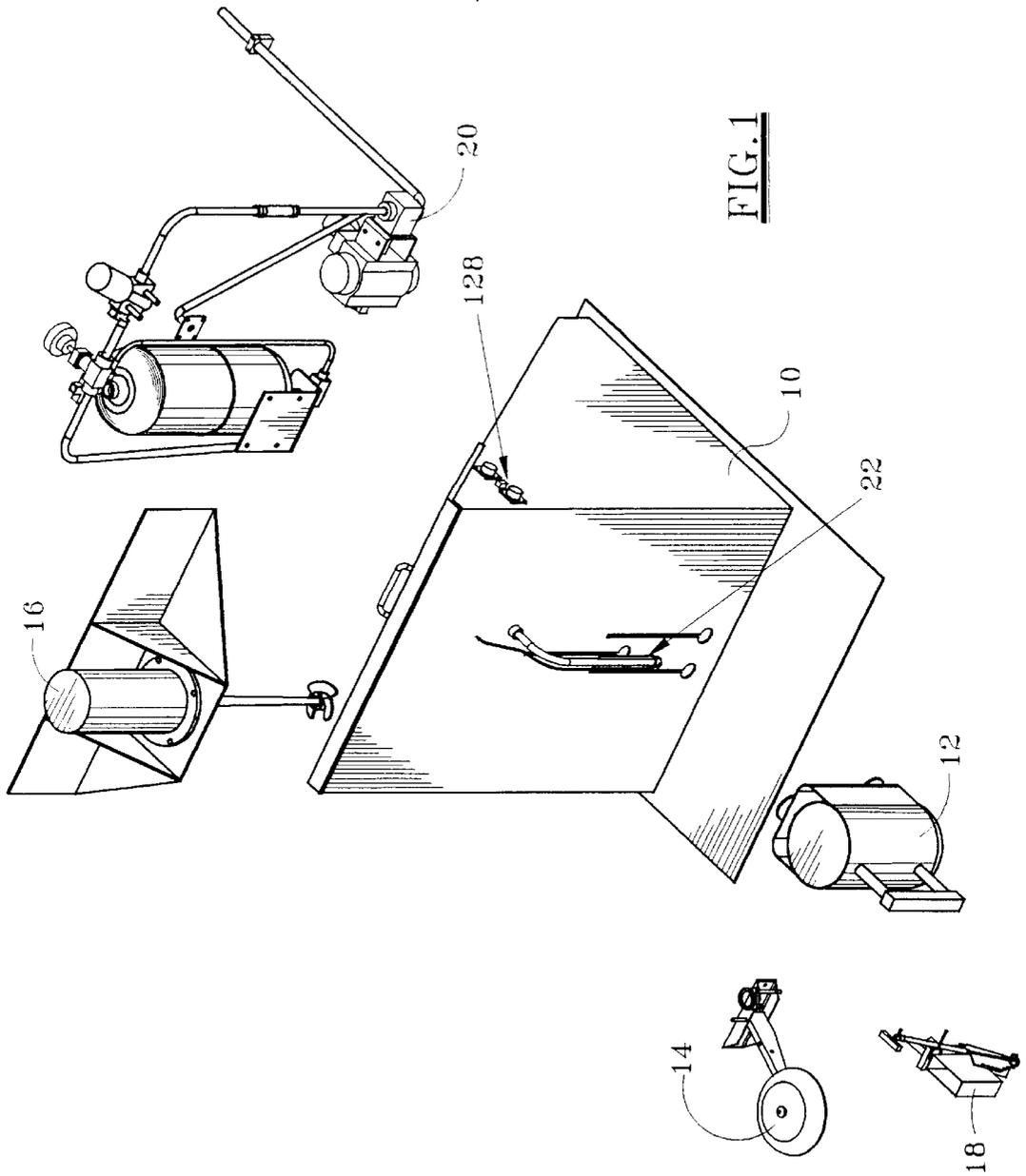
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12 Claims, 19 Drawing Sheets





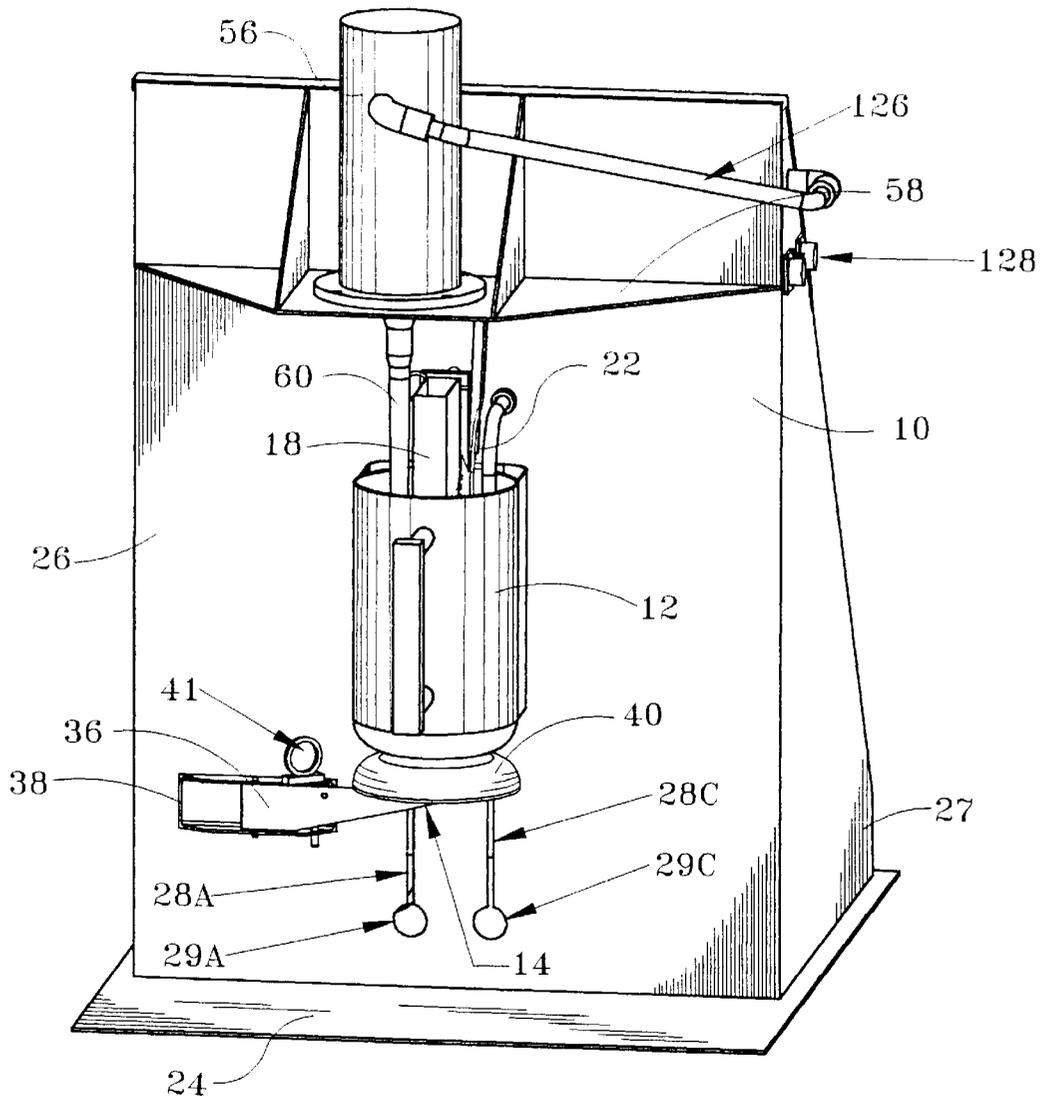
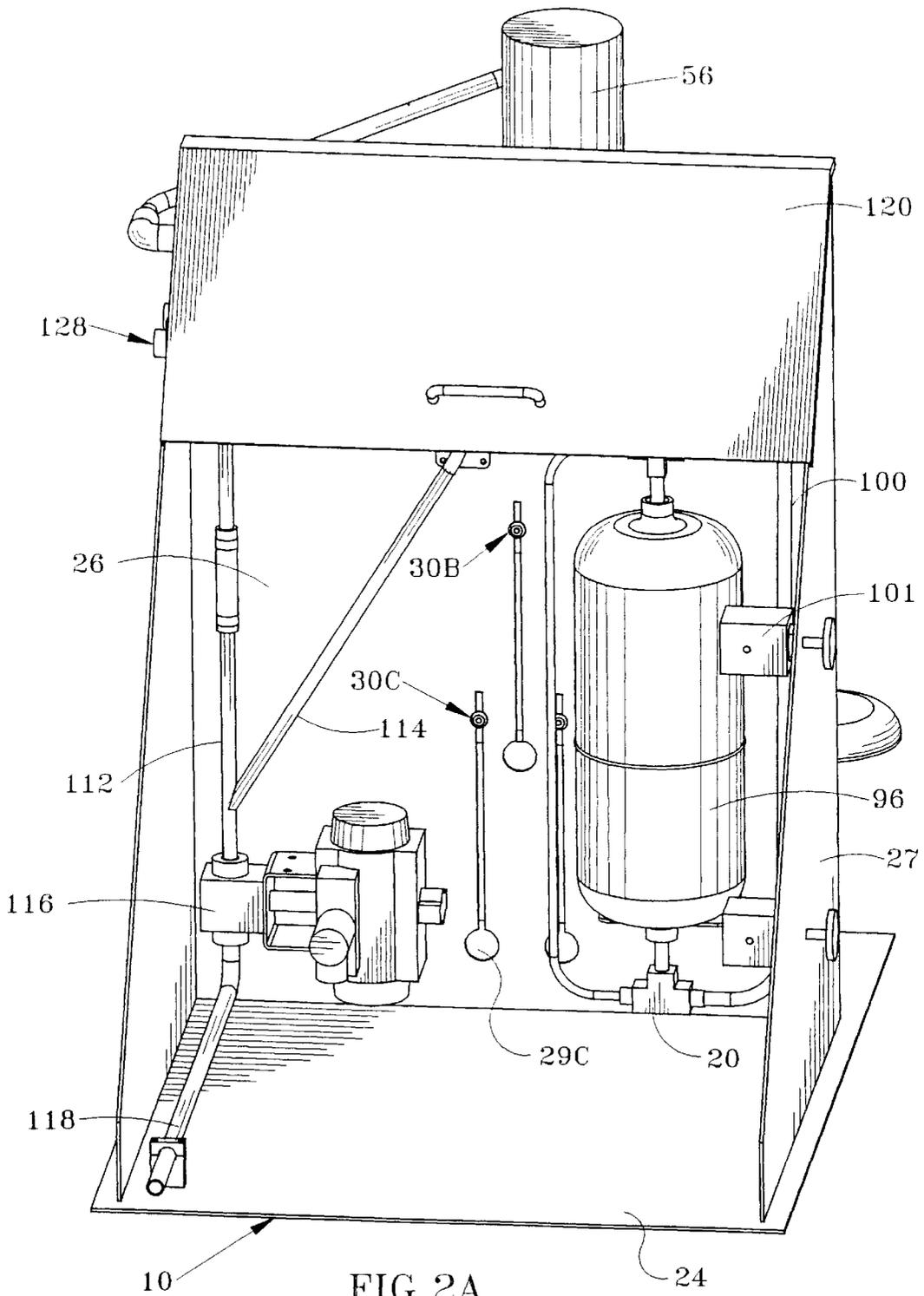


FIG. 2



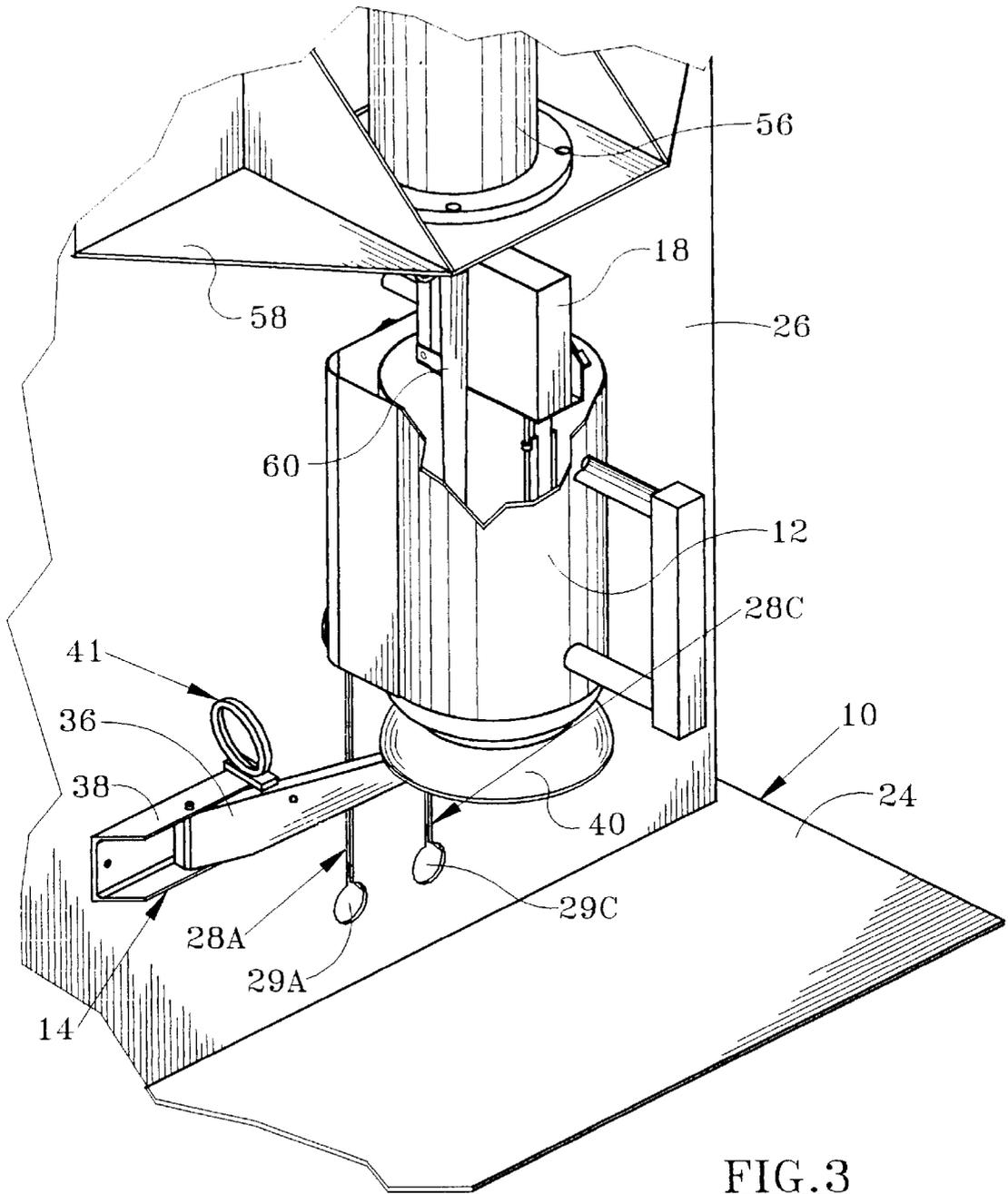
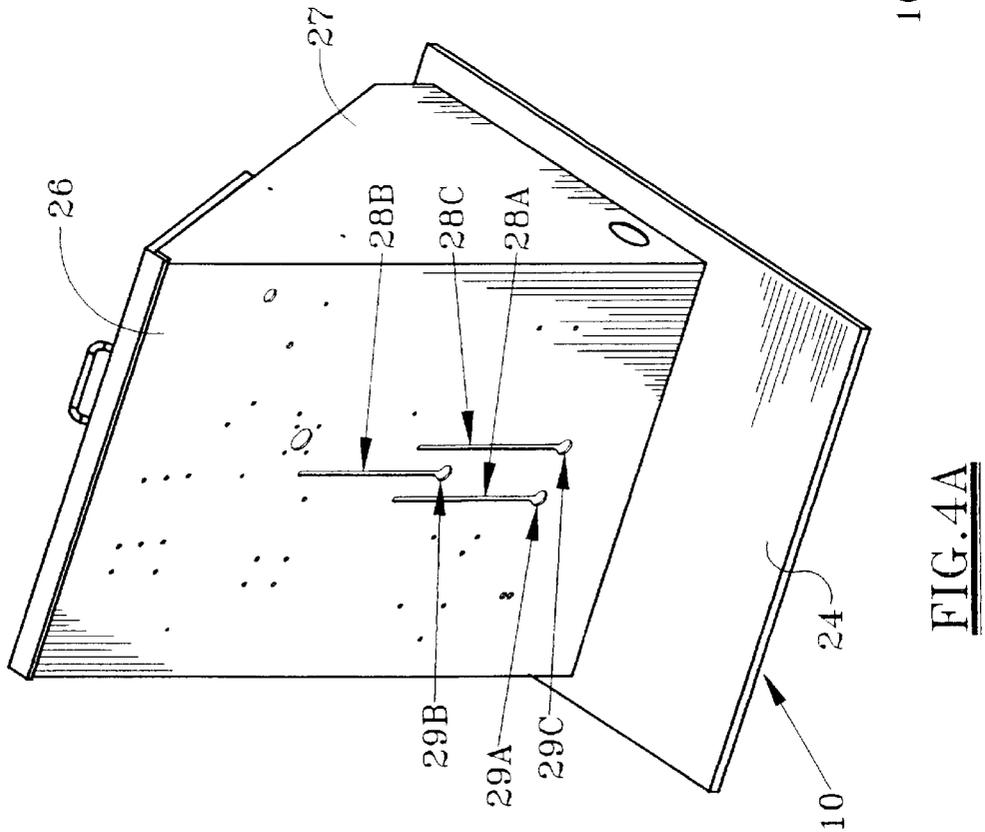
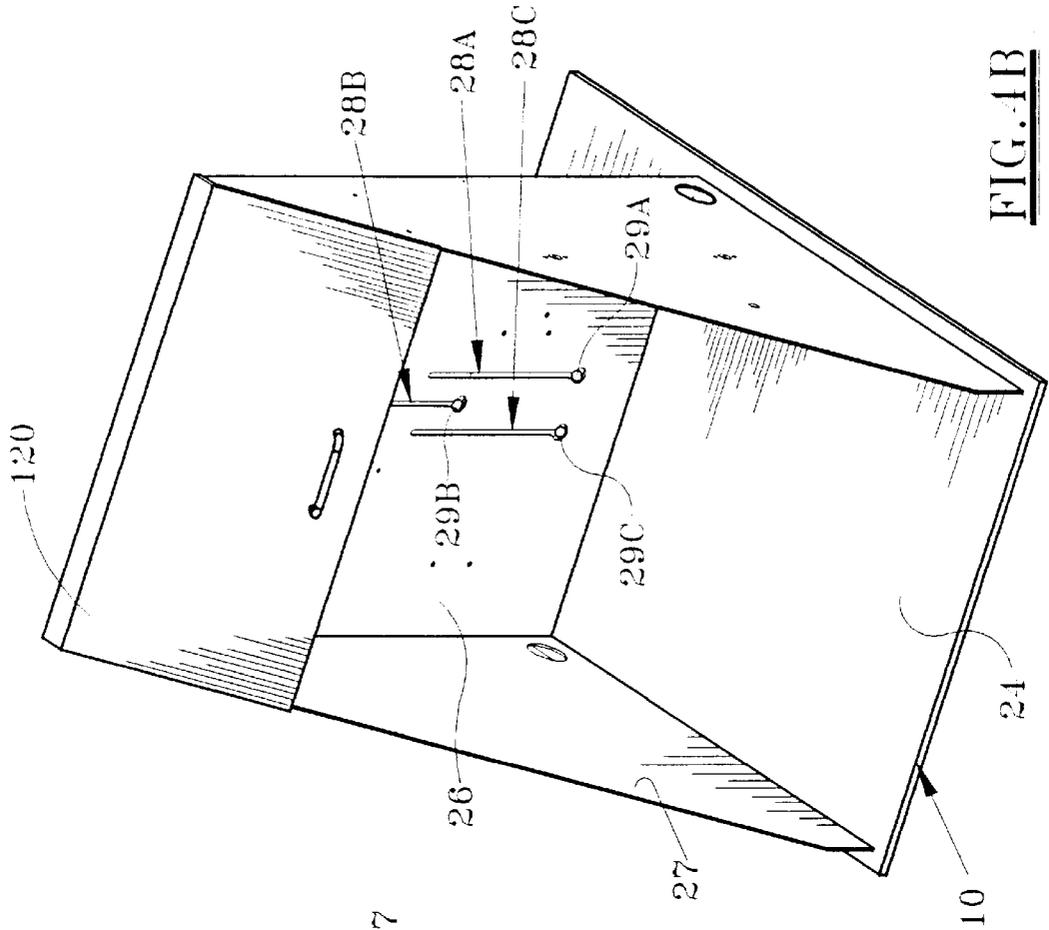


FIG. 3



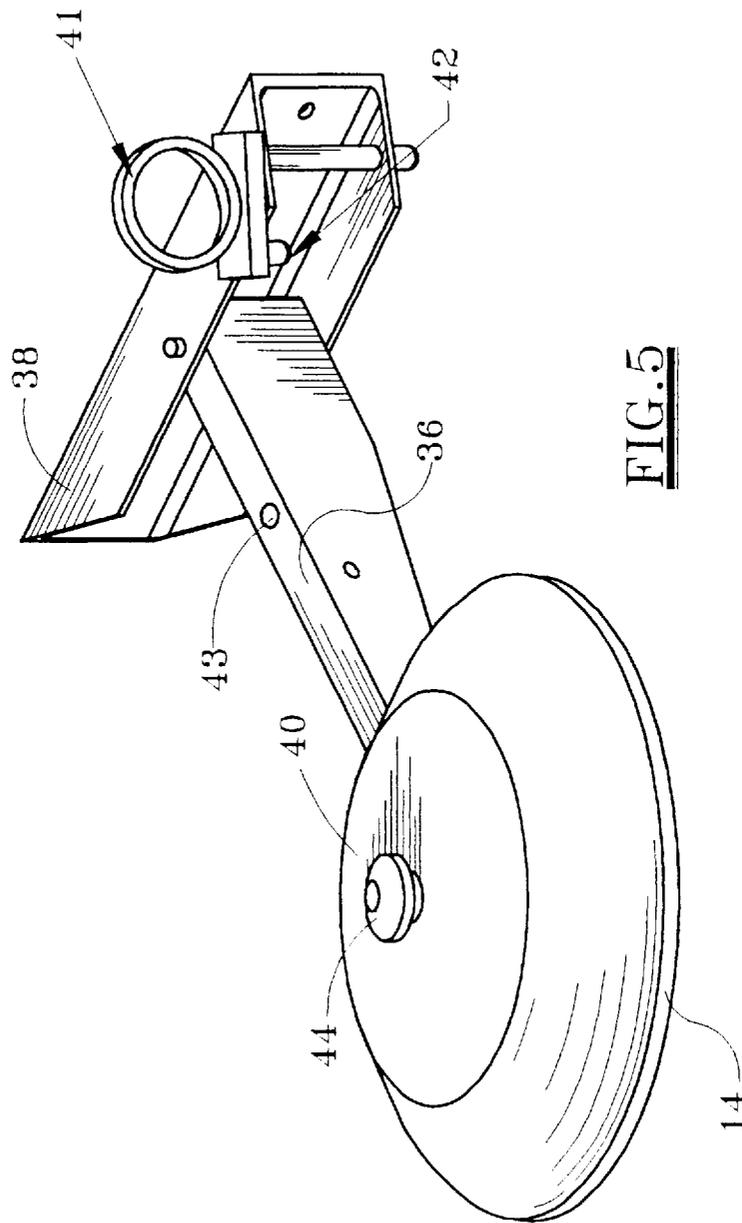


FIG. 5

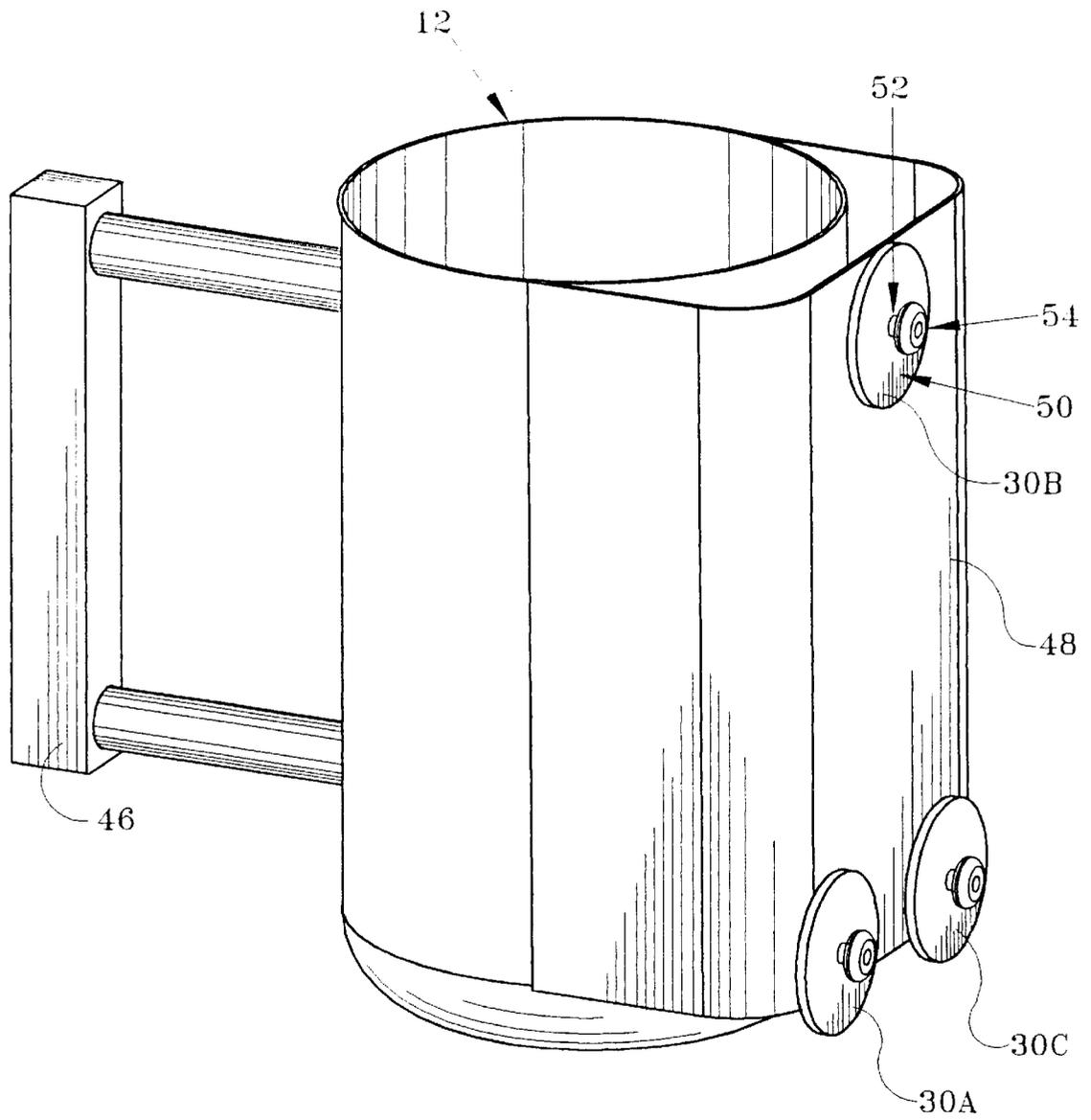


FIG. 6

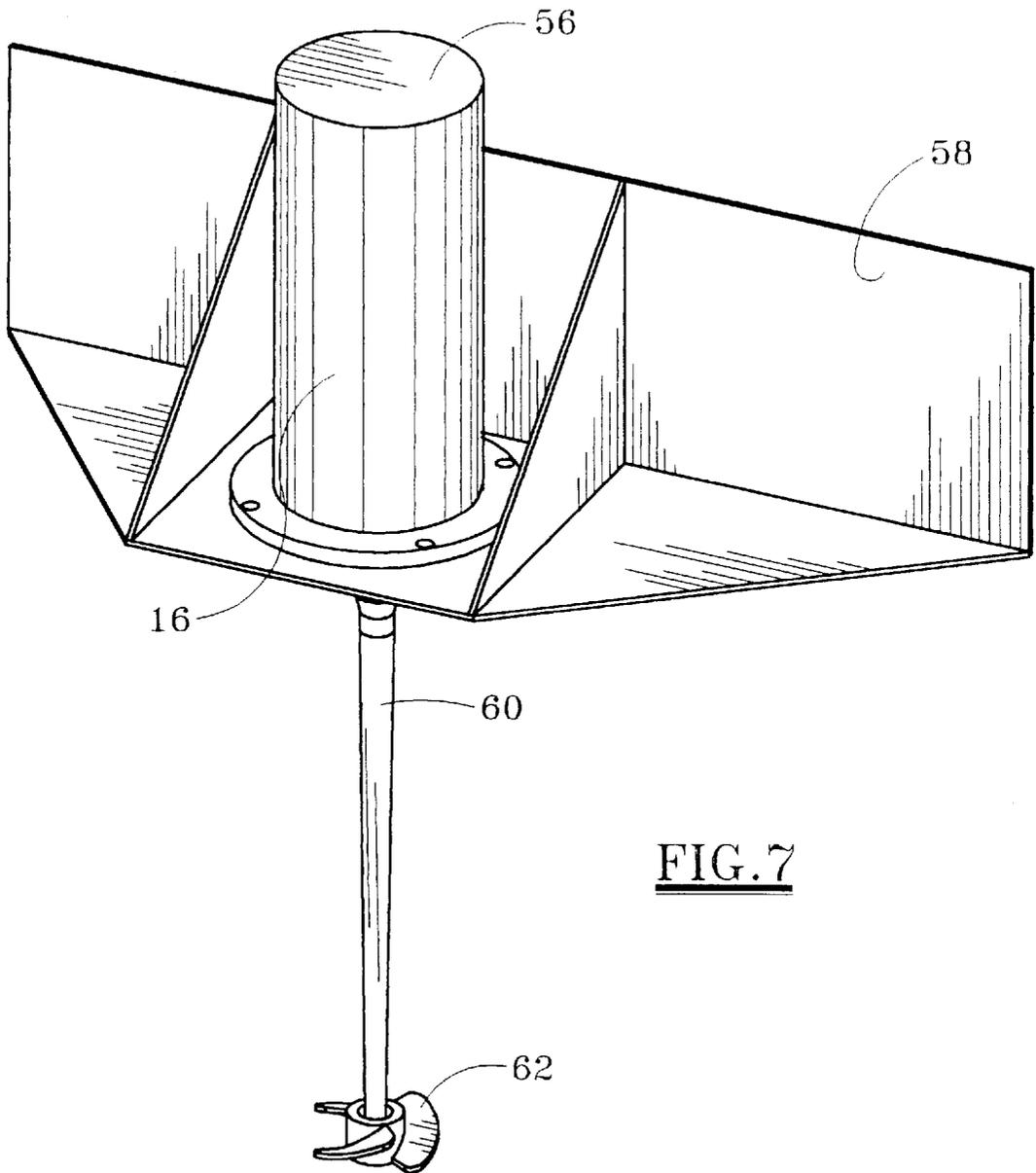


FIG. 7

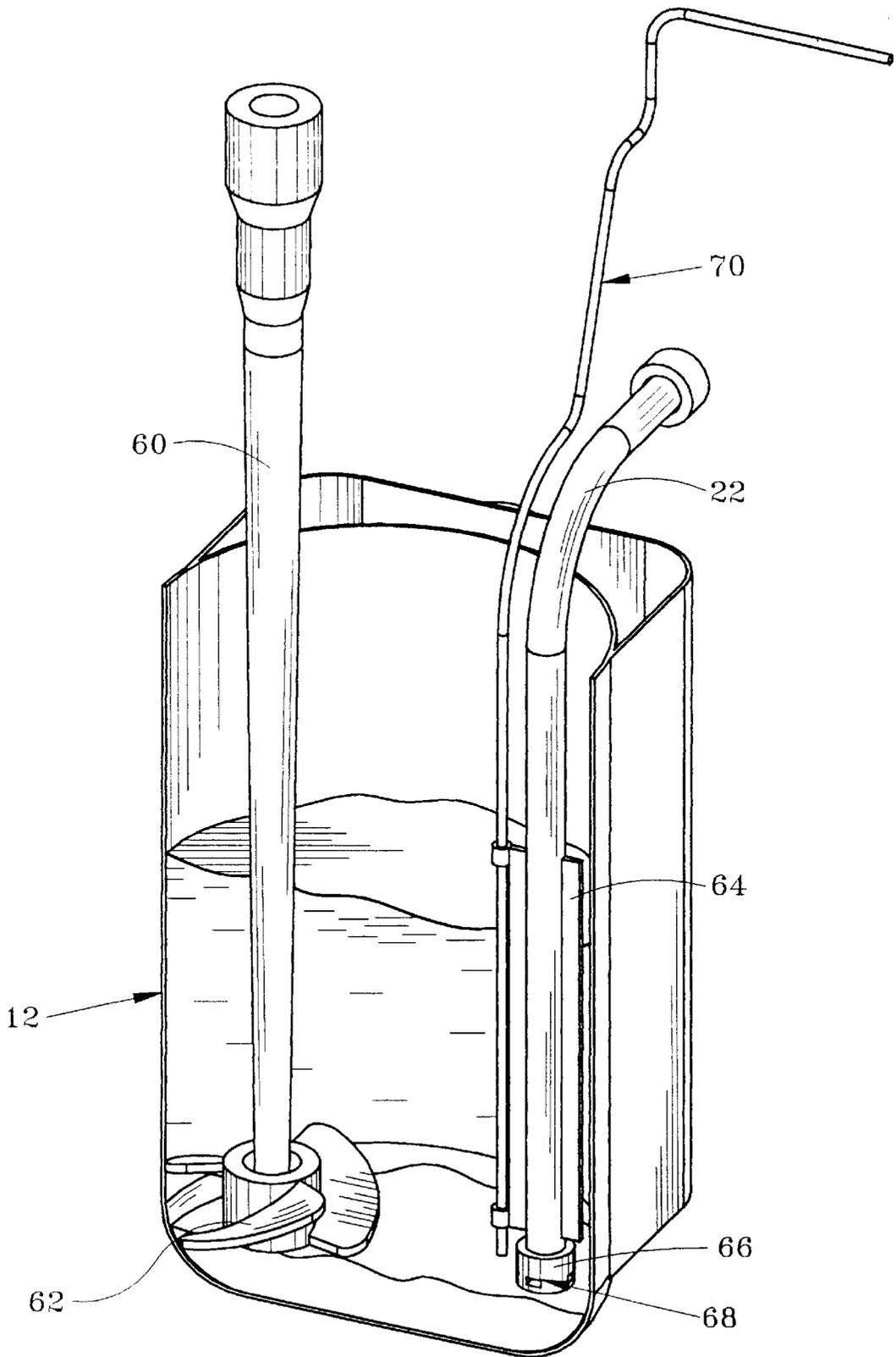


FIG. 8

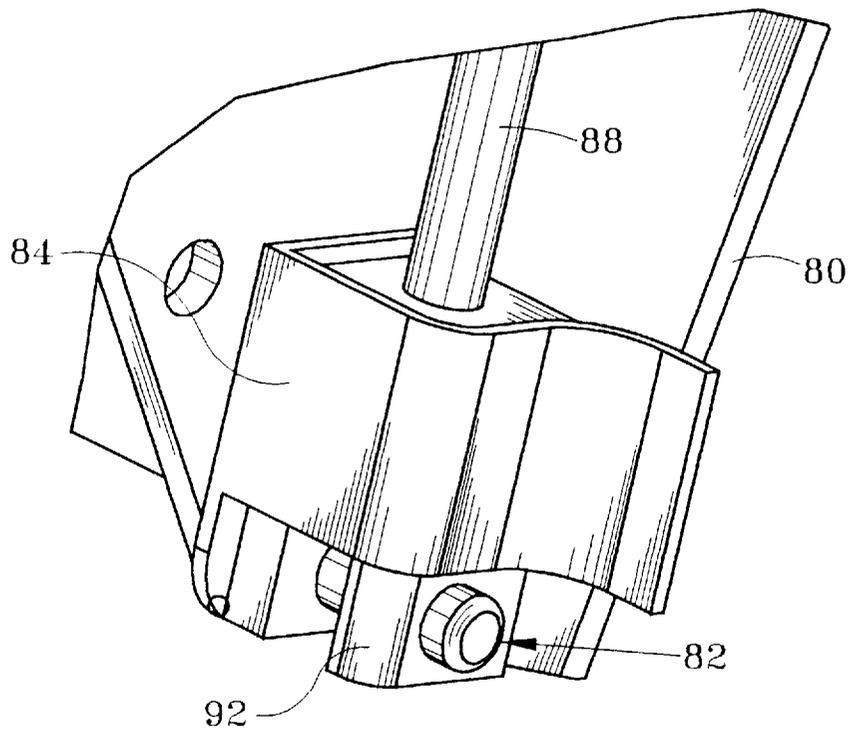


FIG. 9A

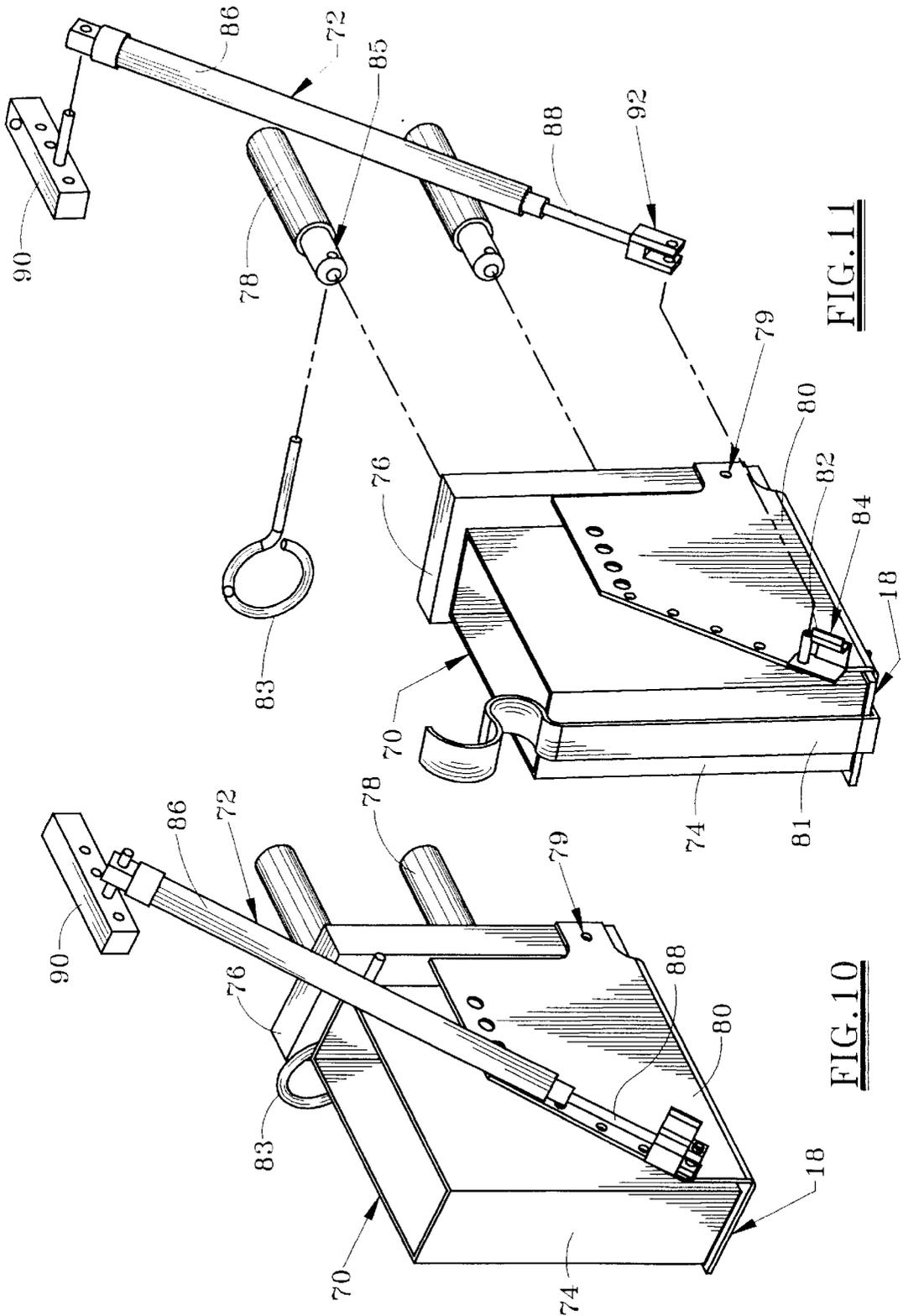


FIG. 11

FIG. 10

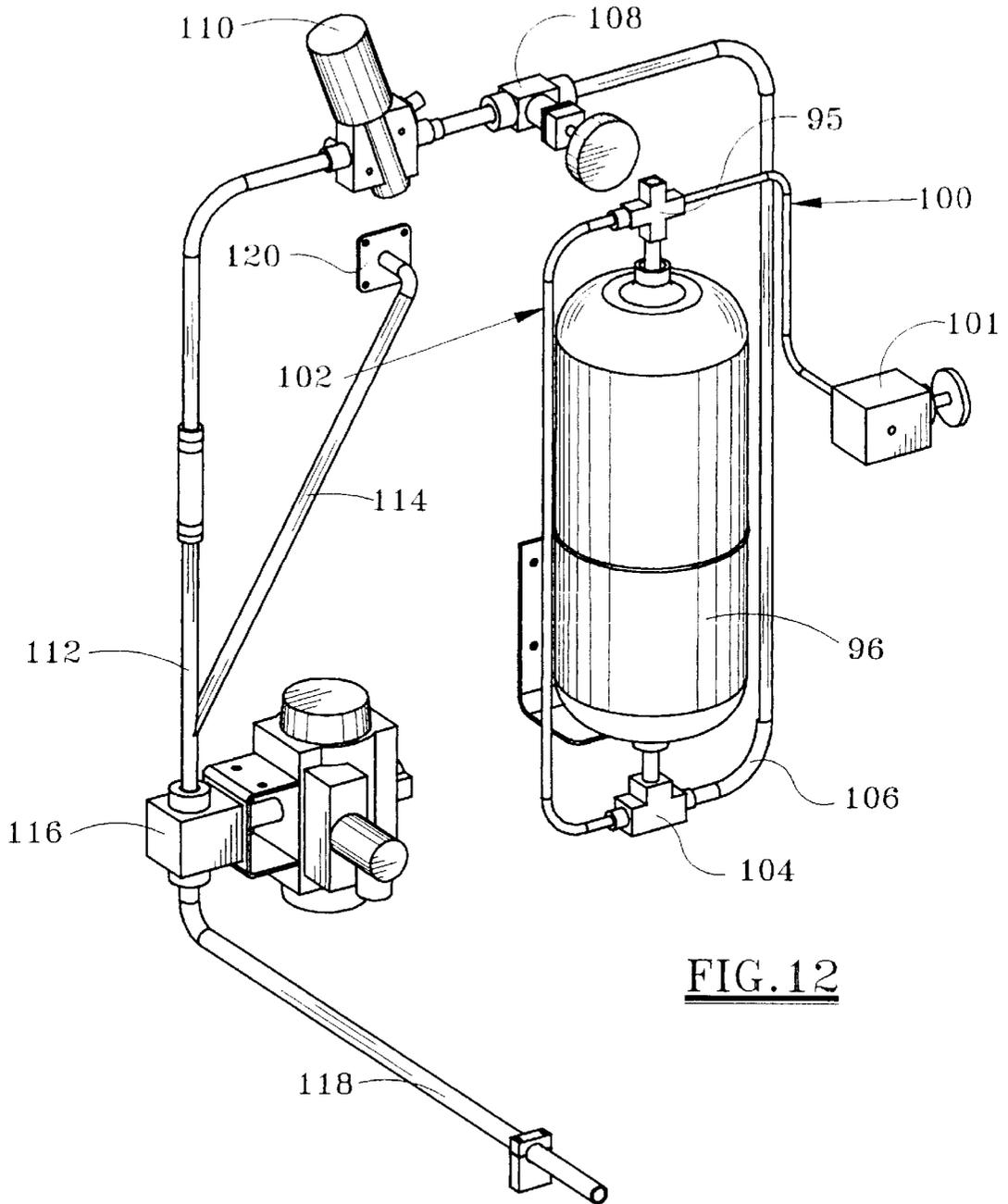


FIG. 12

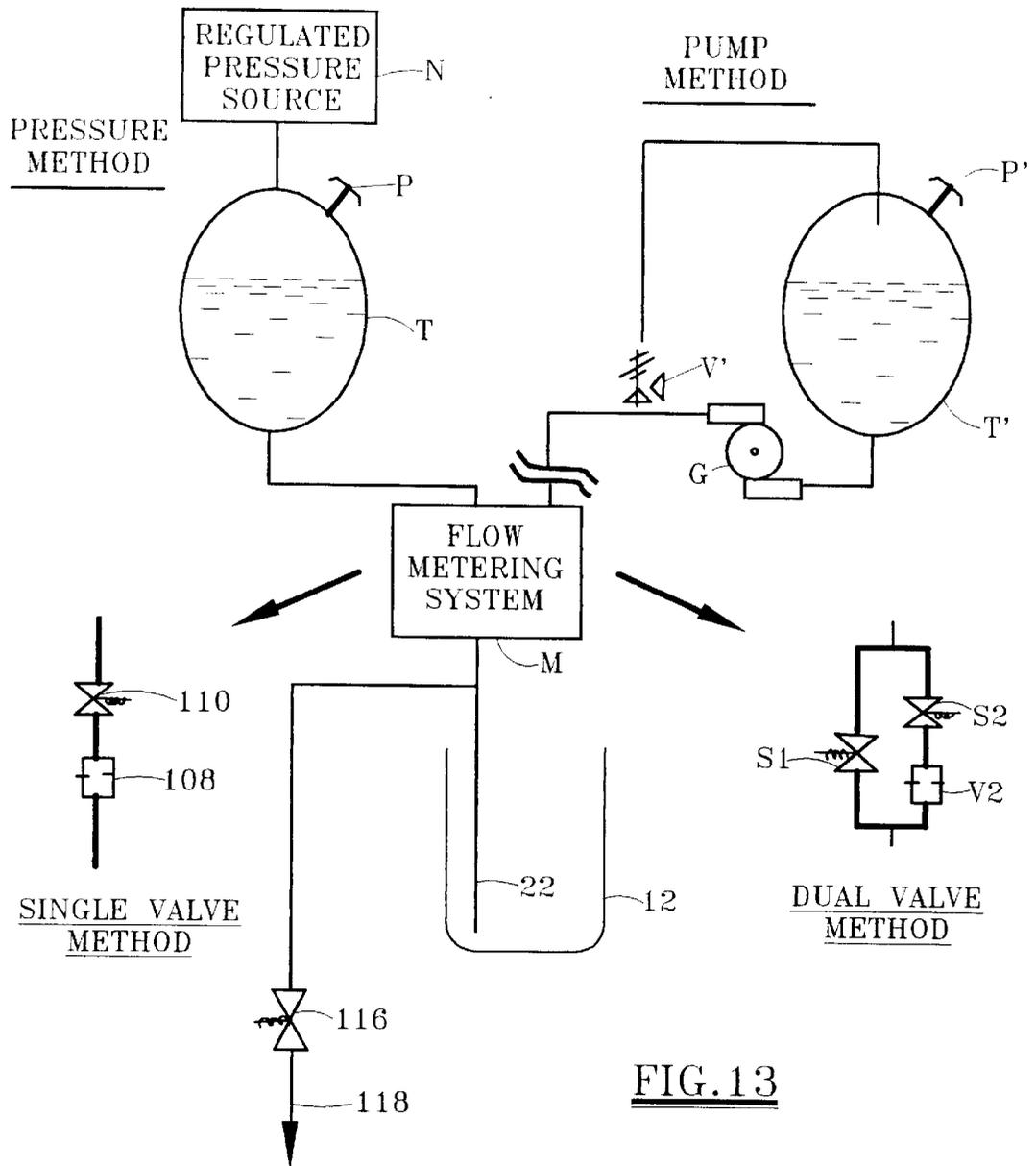
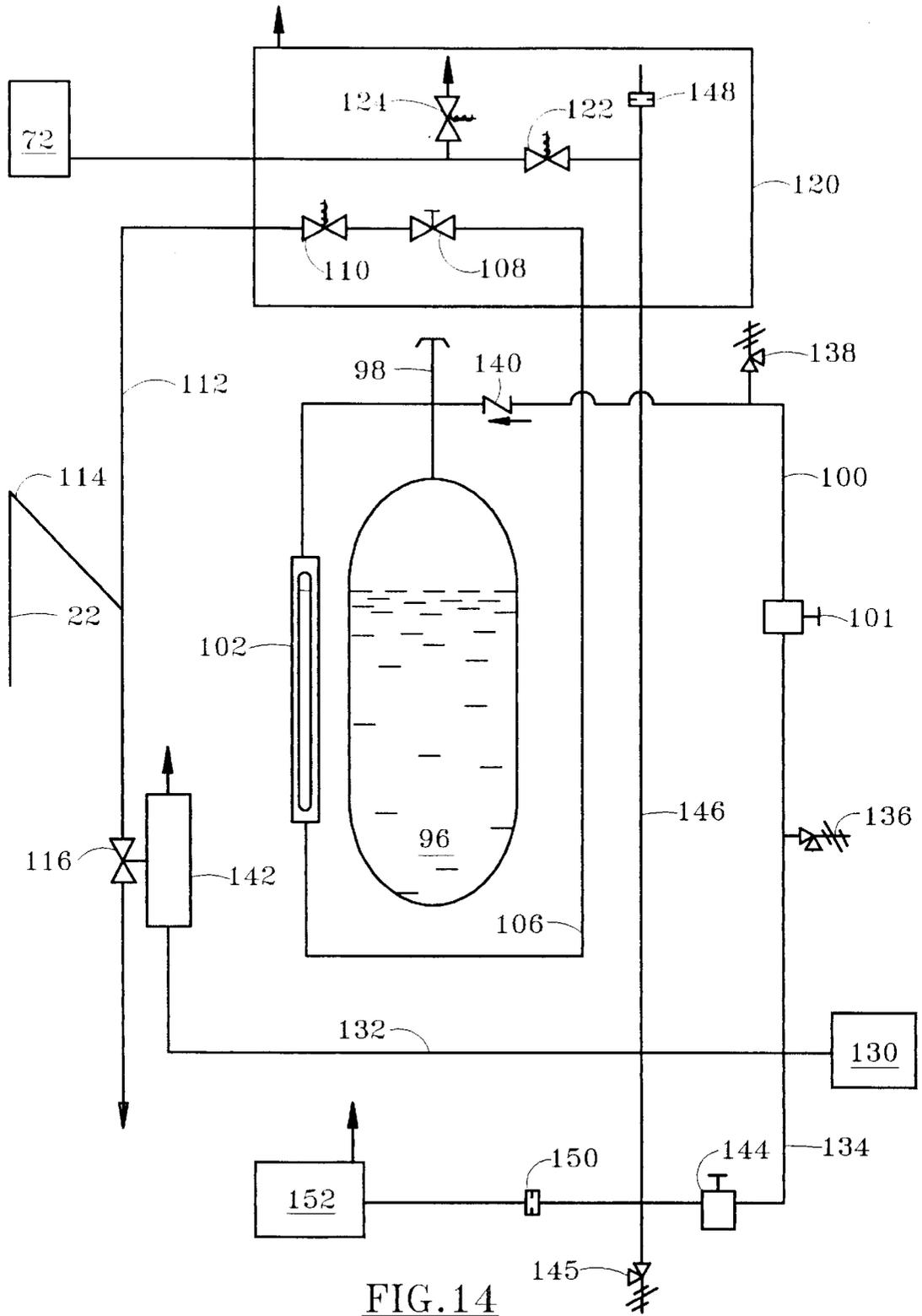


FIG. 13



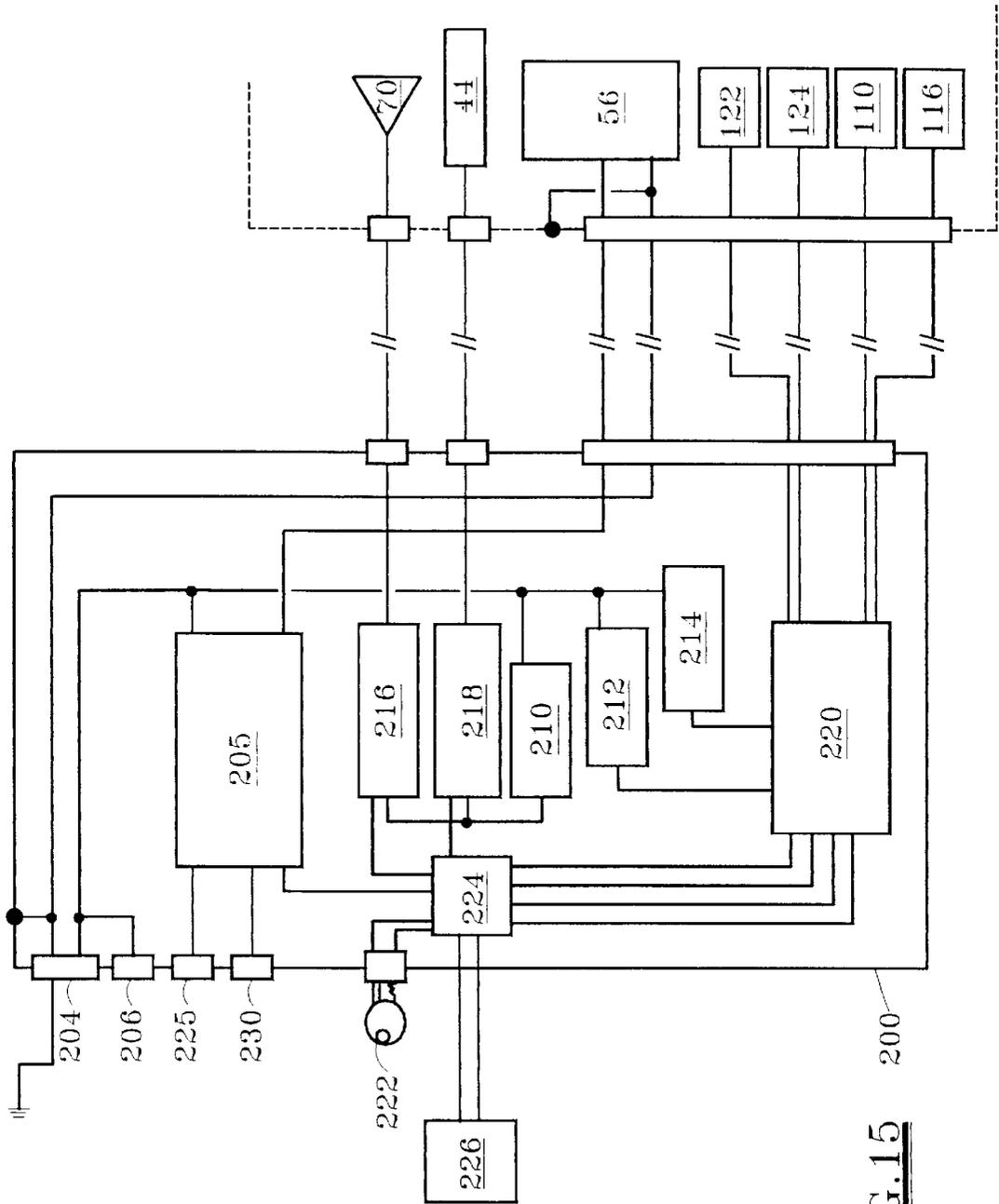


FIG. 15

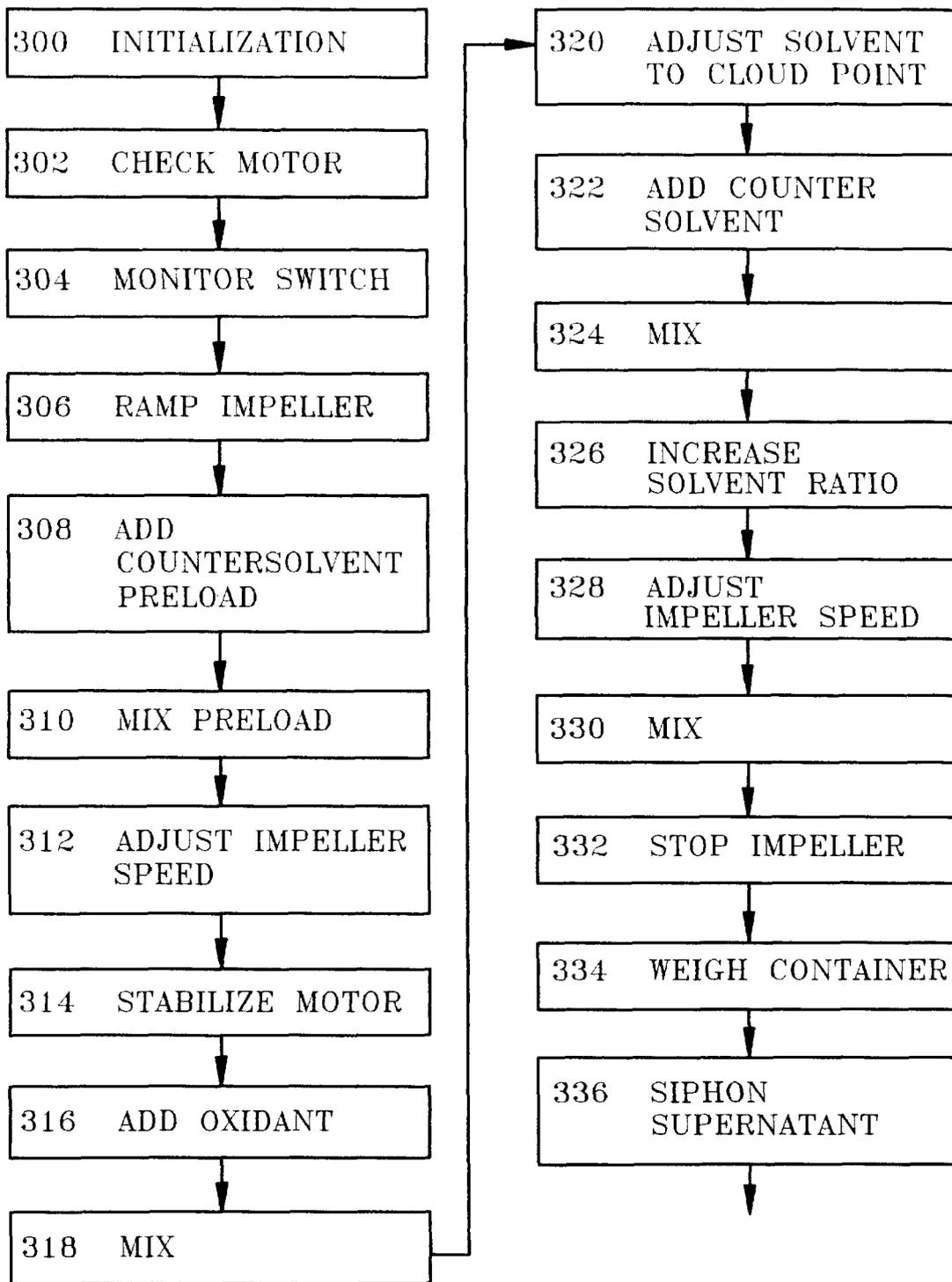


FIG. 16

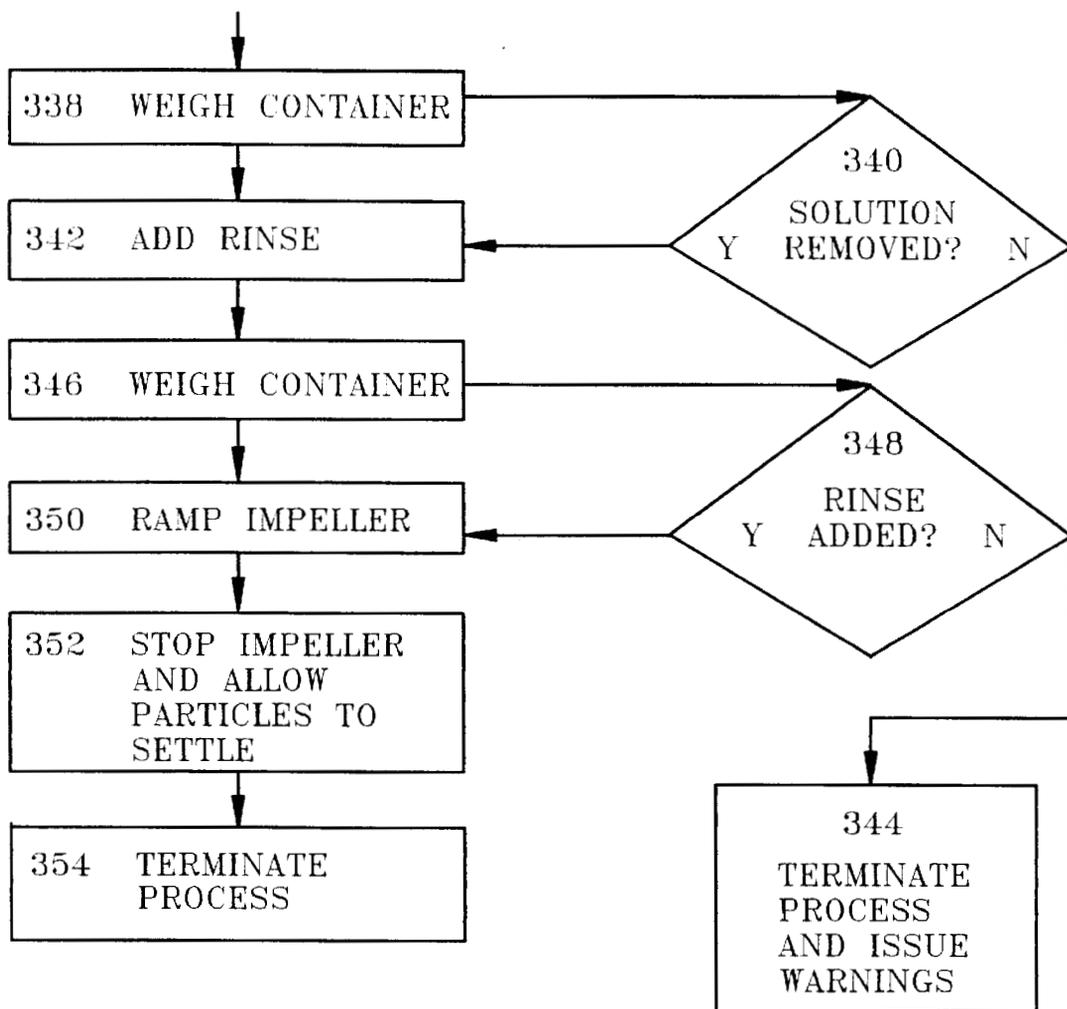


FIG. 16A

TEMPERATURE EFFECT ON BINDER PRECIPITATION

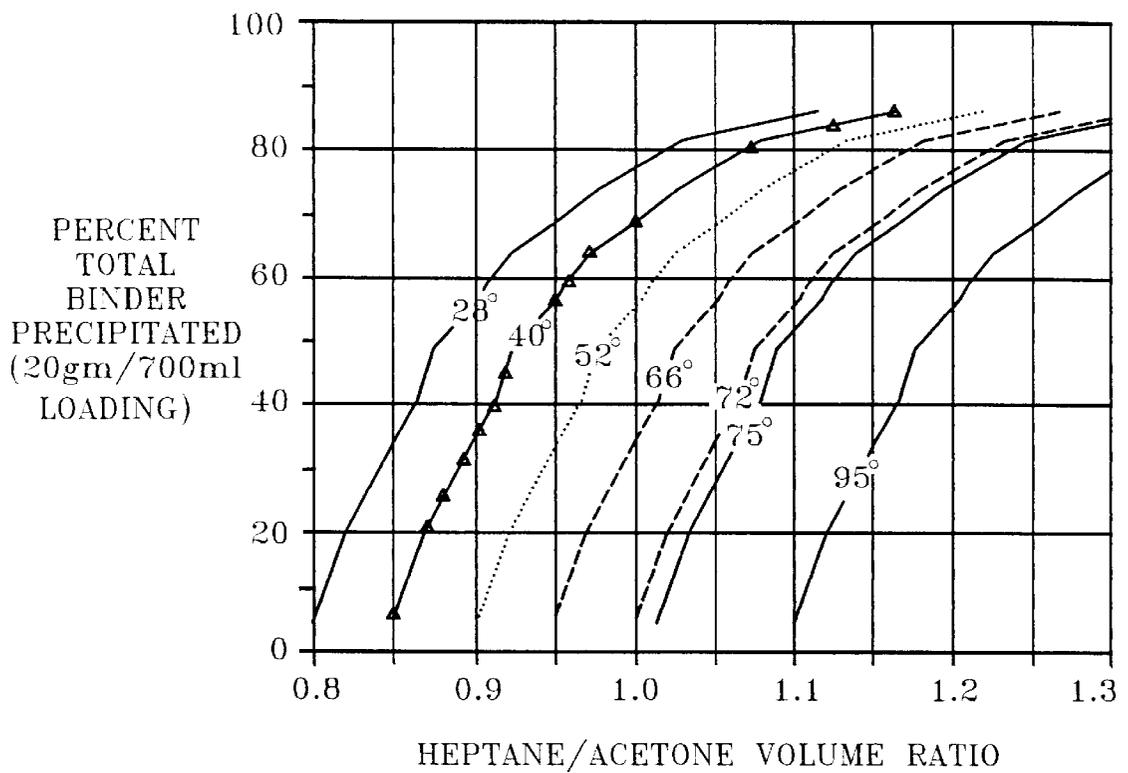


FIG. 17

AUTOMATED PROPELLANT BLENDING

ORIGIN OF THE INVENTION

The invention described herein was made in the performance of work under a NASA contract and is subject to the provisions of Section 305 of the National Aeronautics and Space Act of 1958, Public Law 85-568 (72 Stat. 435; 42 U.S.C. 2457).

FIELD OF THE INVENTION

The present invention relates to apparatus and methodology for blending propellant or explosive mixtures of a fuel and an oxidant with a binder.

BACKGROUND OF THE INVENTION

Pyrotechnic compositions are used for many useful purposes. Such compositions are used in the aerospace industry to provide ignition, propulsion, vehicle separation, and emergency egress. The automotive industry also uses ignition and gas production compositions for occupant restraint systems, i.e. airbags. The demand for these pyrotechnic mixtures continues to grow.

A typical pyrotechnic device is the NASA standard initiator (NSI). The NSI is a two-pin electrically activated, electro-explosive device containing zirconium potassium perchlorate (ZPP) propellant. Initially designed and used in 1966 for the Apollo lunar mission, the standard NSI is still used today in the NASA space shuttle system.

The propellant used in the NSI is a composition of finely divided zirconium, potassium perchlorate and graphite held together with a fluoroelastomer polymer as a binder. The mixture, besides being highly reliable, is very sensitive to ignition stimulus, particularly static discharge. The propellant is an extremely fast brisant explosive. These properties make the manufacture and handling of bulk quantities of ZPP very hazardous.

In the automotive industry, inflatable vehicle occupant restraint systems are standard equipment included in millions of new vehicles every year. Although different propellants are sometimes used in automotive applications, the initiators are very similar to the NSI's in that they usually use a ZPP propellant and are generally activated by electrical stimulation. The manufacture of propellants has been an inherently dangerous task owing to the risk of fire or explosion. The pyrotechnics industry has experienced accidents in the manufacture of energetic compositions, particularly with hand blending techniques. Flare and illumination compositions based on metal fuels such as, for example titanium, aluminum, magnesium and the like, exhibit characteristics similar to ZPP.

The performance of an energetic material such as ZPP is dependent on many factors such as purity, particle size distribution, particle shape, surface area, and the like. One of the factors affecting the reproducibility of the performance of a propellant is the degree of mixing, or homogeneity of the blend. A pyrotechnic composition that has been poorly mixed often exhibits slower burn rates and is less dependable than a well-mixed one. Some pyrotechnic compositions make use of a binder system that serves as an adhesive, holding the fuel and oxidant in a well-mixed condition. Without a binder many compositions separate under the influence of gravity or vibration, resulting in performance degradation. Therefore, proper mixing and incorporation of the binder during manufacture are key process parameters.

Heretofore, the blending of the NSI propellant ingredients has been done by hand, typically using a solvent evaporation

procedure. The propellant components were generally poured in the form of dry powders into a 45 degree inclined bowl rotating with a solution of the binder (fluoropolymer in acetone or n-butyl acetate, for example). Manipulating the blend for homogeneity, the solvent was evaporated to leave the binder and obtain a moist solid. The moist solid was then sieved in air through a screen, often by hand. The screened propellant composition was then dried to remove the residual solvent. This process has produced good propellant, but has a number of disadvantages. The solvent evaporation technique relies on manual and frequent movement of the mix during processing to achieve good blends. Thus, the outcome of the blend is very dependent on the skill of the person doing the blending. The solvent evaporation method can also be very dangerous. Fire and explosion have occurred during the solvent evaporation blending process. The operator is in close proximity to the mixing and granulation process, a high risk situation. The evaporation method is also time intensive, requiring several hours per blend.

The preparation of propellants has also been done using a precipitation technique. In this method, the fuel and oxidizer components are suspended in the binder solution by a mechanical mixer and a countersolvent is added while mixing the solution. The countersolvent causes the binder to precipitate from the solvent. As the binder precipitates, the active particles are entrapped in the binder. This process has historically been a manual operation with the operator in close proximity to the mix container, adding the dry components and countersolvent. The timing of process events lacked a degree of repeatability due to the human operator. Previous attempts to use the precipitation methodology for the preparation of propellants resulted in poor repeatability. These blends have suffered from rubbery inclusions, or the formation of clay-like products that require granulation similar to the evaporation process. Fire and explosion have also occurred during the precipitation blending process. These incidents have usually been due to pyrophoric or static discharge ignition of the metal fuel component. The operator has also been at risk in close proximity to the mixing process which involves the use of volatile, flammable solvents, as well as the propellant particles.

From the descriptions above it is evident that the largest factor reducing personnel safety is close proximity to the blending operation. The ability to perform the blending operation from a remote location would greatly increase safety. It would be desirable to have an automated propellant blending system in which the quality and characteristics of the propellant composition are not so dependent upon the skill of the human blending operator. It would also be desirable to speed up production and expand the capacity of propellant manufacturing facilities. It would be further desirable to have available a propellant blending system which avoids the evaporation method and the safety hazards incidental to drying the propellant composition to dryness. It would also be desirable to use a propellant blending process which minimizes the screening requirement and obtains a finer end product than has been available heretofore. Ideally, an automated propellant blending system would be able to produce agglomerated propellant particles having a controlled particle size distribution.

SUMMARY OF THE INVENTION

We have invented an automated propellant blending system using a closely metered addition of a countersolvent to a solution of binder with fuel, oxidant and other particles suspended therein to achieve a precise precipitation rate of the binder during a precipitation cycle. By establishing a

profile of binder precipitation versus the ratio of countersolvent to solvent, for example, using ordinary laboratory equipment to precipitate fixed amounts of binder solution and various countersolvent-solvent ratios and temperatures, a curve and/or computer algorithm can be derived to precisely control countersolvent addition near the cloud point or coacervation point to obtain a controlled rate of precipitation of the binder into the mix. This assures a continuous, predictable release of binder precipitate into the mix container for a controllable transition of the properties of the binder during agglomeration and finishing of the propellant composition particles. The system can include remote, computer-controlled precipitation for safety, reliability and improved product properties.

In one aspect, the present invention provides a method for preparing a solid propellant mixture of oxidant and fuel particles in a binder. The method includes the steps of:

- (a) admixing solid particles in a solution of binder;
- (b) adding countersolvent to the admixture of step (a) to about a coacervation point while maintaining agitation;
- (c) metering countersolvent under controlled conditions of shear into the mixture of step (b) to precipitate the binder and form aggregated particles, wherein the countersolvent metering rate and shear rate are matched to obtain a desired particle size distribution of the aggregated particles;
- (d) admixing excess countersolvent into the mixture from step (c), preferably at a higher countersolvent addition rate relative to step (c), while maintaining conditions of shear;
- (e) maintaining agitation of the mixture from step (d) for a period of time to allow the binder in the aggregated particles to harden;
- (f) rinsing the hardened aggregated particles from step (e) with additional countersolvent.

The method is particularly applicable to the preparation of metal powder/oxidant/polymer propellant blends, especially zirconium-potassium perchlorate propellant blends using a fluorinated elastomer such as a terpolymer of hexafluoropropylene, vinylidene fluoride and tetrafluoroethylene. The method can also be used to coat any particles in general with a polymeric binder. For example, the method can be used to coat metallic particles to inhibit air oxidation during storage.

Steps (a) and (b) preferably include charging a mixing container with the binder solution, fuel particles, optional processing aids such as graphite and a countersolvent preload, mixing the contents of the mixing container, and while maintaining mixing of the mixing container, adding a charge of oxidant particles to the mixing container. The addition of the oxidant particle charge, as well as the countersolvent addition and hardening of the aggregated particles, can be remotely actuated to facilitate personnel safety.

In a preferred embodiment, the method includes empirically determining the coacervation point for the countersolvent-solvent system as a function of temperature. Based on this empirical determination, the countersolvent ratio of the coacervation point relevant to step (b) is estimated. Step (b) preferably includes the sequential steps of adding a preload of countersolvent to avoid coacervation, preferably to within about 20 percent of the countersolvent-solvent ratio at the coacervation point, allowing the admixture to thermally equilibrate, measuring the temperature of the admixture, calculating the countersolvent-solvent ratio needed for coacervation at the measured temperature, and

adding additional countersolvent to the mixture to make the calculated ratio of countersolvent to solvent.

The countersolvent metering ratio in step (c) is different from a ratio of countersolvent addition in step (b), typically slower in step (c) relative to step (b) to avoid precipitating the binder too quickly. In step (c), the countersolvent metering can be stopped and shearing of the mixture maintained for a period of time effective to aggregate the particles to the desired particle size distribution while the particles have a tendency to stick together, prior to adding the excess countersolvent and hardening the aggregated particles in steps (d) and (e).

The rinsing step (f) can desirably include stopping agitation of the mixture and allowing the aggregated particles to settle, decanting supernatant, and adding additional countersolvent.

In another aspect, the present invention provides apparatus for manufacturing a solid propellant mixture of oxidant and fuel particles in a binder. The apparatus includes a mixing container, a variable-speed impeller, a countersolvent supply system, a decanting line and a control system. The impeller is provided for agitating a mixture of binder, solvent and solid particles in the mixing container. The countersolvent supply system is provided for adding countersolvent into the mixing container. The decanting line is provided for removing supernatant liquid from the mixing container. The control system is capable of adjusting the speed of the impeller, adjusting the rate of countersolvent addition and actuating liquid removal from the mixing container through the decanting line. The control system preferably includes a countersolvent metering routine for effecting the steps of: (1) adding the countersolvent to the mixing container with operation of the mixing impeller up to about a coacervation point, (2) at about the coacervation point, matching the countersolvent addition rate and impeller speed to obtain a desired particle size distribution of the particles aggregated with the binder, and (3) thereafter adding excess countersolvent to the mixing container, preferably by increasing the countersolvent addition rate. The control system also preferably includes a liquid removal routine for stopping the impeller, allowing particles to settle in the mixing container and actuating a valve in the decanting line to remove supernatant liquid from the mixing container.

The countersolvent supply system preferably includes relatively high and low countersolvent flow modes. In one embodiment, the countersolvent supply system includes first and second parallel flow paths. The first flow path is sized for a relatively rapid flow of countersolvent relative to a flow resistance of the second path. The second path is generally used for the countersolvent addition during step (2) in the countersolvent metering routine. In an alternate embodiment, a single valve in a flow path is operable for the high countersolvent flow mode in a continuously open position, and capable of being pulsed open and closed at a frequency selected to provide a desired low countersolvent flow mode rate.

The apparatus preferably includes a weight sensor for measuring changes in the weight of the mixing container. The liquid removal routine can include a comparison of the mixing container weight before and after actuation of the valve to confirm removal of the supernatant liquid. The control system preferably includes a final countersolvent addition routine for adding additional countersolvent to the mixing container after execution of the liquid removal routine, comparing the mixing container weight before and after the additional countersolvent addition to confirm the

countersolvent addition, and stirring the mixing container with the impeller.

The apparatus also preferably includes a temperature sensor such as a thermocouple for measuring the temperature of the mixing container. Step (1) of the countersolvent metering routine can include adding a preload of countersolvent to within about 20 percent of the coacervation point, measuring the temperature of the mixing container, calculating the countersolvent-solvent ratio of the coacervation point at the measured temperature, and adding additional countersolvent to the mixing container to make the calculated ratio of countersolvent to solvent.

The apparatus can also include a dump mechanism which is remotely actuatable to add a supplemental charge of particles to the mixing container, for example, oxidant particles. The countersolvent supply system preferably includes a tank including a charge of countersolvent. The apparatus can also include a charge of fuel particles in a binder solution in the mixing container. Preferably the fuel is zirconium, the oxidant is potassium perchlorate and the binder is fluoroelastomer.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is an exploded view of an embodiment of the propellant blending system according to the present invention.

FIG. 2 is a perspective front view of the blending system of FIG. 1.

FIG. 2A is a perspective rear view of the blending system of FIG. 2.

FIG. 3 is an enlarged perspective front view, with the container assembly partially cut away to show the dump mechanism, of a portion of the blending system of FIG. 2.

FIGS. 4A and 4B are perspective front and rear views, respectively, of the chassis assembly of the propellant blending system of FIG. 1.

FIG. 5 is a perspective view of the platform assembly of the propellant blending system of FIG. 1.

FIG. 6 is a perspective view of the container assembly of the propellant blending system of FIG. 1.

FIG. 7 is a perspective view of the motor assembly of the propellant blending system of FIG. 1.

FIG. 8 is a perspective view of the container assembly, cut away to show the impeller, dip tube, liquid level and settled particles in the propellant blending process using the apparatus of FIG. 1.

FIG. 9 is a perspective view of the dump mechanism of the propellant blending system of FIG. 1, shown in the open position.

FIG. 9A is an enlarged detail of the dump mechanism of FIG. 9.

FIG. 10 is a perspective view of the receptacle assembly of the dump mechanism of FIG. 9, shown in the closed position.

FIG. 11 is an exploded view of the dump mechanism of FIG. 9.

FIG. 12 is a perspective view of the countersolvent supply system of the propellant blending system of FIG. 1.

FIG. 13 is a schematic diagram showing alternative countersolvent supply methods for the propellant blending system of the present invention.

FIG. 14 is a flow schematic of the propellant blending system of FIG. 1.

FIG. 15 is a schematic diagram of a control system for the propellant blending system of FIG. 1.

FIG. 16 is a typical propellant blending process software flowchart according to an embodiment of the invention.

FIG. 17 is a graph of Viton B fluoropolymer precipitation from acetone using heptane versus countersolvent-solvent ratio at various temperatures at a loading of 20 g/700 ml.

FIG. 18 is a graph of the coacervation point of the countersolvent-solvent ratio of Viton B fluoropolymer in acetone and heptane at a loading of 20 g/700 ml.

DETAILED DESCRIPTION

With reference to the accompanying drawings wherein like numerals are used to designate like parts, in one embodiment taking advantage of the principles of the present invention, a propellant blending system is provided in the form of a generally self-contained chassis assembly 10 on which are mounted container assembly 12, platform assembly 14, motor assembly 16, dump mechanism 18, countersolvent supply system 20 and dip tube 22. Chassis assembly 10 (see FIGS. 4A and 4B) includes a horizontal base 24, vertical partition 26 and opposite side-wall supports 27. The components of the propellant blending system are generally mounted on the vertical partition 26, as will be described in more detail below, with appropriate connections for the supply of electricity, instrument air, nitrogen, countersolvent and the like as necessary. Vertical slots 28A, 28B and 28C with enlarged lower ends 29A, 29B, 29C are formed in the partition 26 for receiving respective lugs 30A, 30B and 30C on container assembly 12 (see FIG. 6) for vertically positioning the container assembly 12.

As best seen in FIG. 5, the platform assembly 14 includes a hinged arm 36 secured to the partition 26 by means of bracket 38. The arm 36 is fixed vertically and swings in a horizontal direction to position a support 40 secured at an outer end thereof underneath the container assembly 12 (see FIG. 2). A spring-biased pin assembly 41 mounted in the bracket 38 has a pin 42 receivable in a bore 43 formed in the arm 36 for locking the arm 36 in position to support the container assembly 12. The support 40 can include a load cell 44 for measuring the weight of the container assembly 12 and the contents thereof. Thus, the container assembly 12 is supported on the support 40 for operation of the propellant blending system, but can be removed by removing the pin 42 from the bore 43 and pivoting the arm 36 outwardly to remove the support 40 to allow the container assembly 12 to be moved downwardly by sliding the lugs 30A, 30B, 30C in the respective slots 28A, 28B and 28C.

As best seen in FIG. 6, the container assembly 12 is generally cylindrical with an open top and provided with a handle 46 on one side thereof. On the opposite side, a mounting armature is affixed and includes a generally vertical plate 48 to which the lugs 30A, 30B, 30C are mounted. The lugs 30A, 30B, 30C generally include a base 50 welded or bolted to the vertical plate 48, axle 52 extending outwardly therefrom, and terminating with an enlarged head 54. The lugs 30A, 30B, 30C are generally spaced apart laterally to correspond with the spacing between the slots 28A, 28B, 28C, and at least one of the lugs is preferably offset vertically, as lug 30B, for example. The lugs 30A, 30B, 30C are generally arranged so that the pattern thereof corresponds with the pattern of the open ends 29A, 29B, 29C of the slots 28A, 28B, 28C. The axles 52 have a diameter or width which is less than that of the corresponding slots 28A, 28B, 28C. Each head 54 has a diameter which is larger than the respective slot 28A, 28B, 28C, but smaller than the enlarged ends 29A, 29B, 29C.

As best seen in FIG. 7, the motor assembly 16 includes a motor 56 which can be mounted to the partition 26 (FIG. 2)

by means of bracket **58**. For use with flammable solvents and/or reactive particles, the motor **56** should be explosion proof. A shaft **60** depends from the motor and has a propeller **62** attached at a lower end thereof. As seen in FIG. **8**, the motor assembly **16** is mounted on the partition **26** so that it is positioned to stir the contents of the container assembly **12**. The countersolvent dip tube **22** passes horizontally through the partition **26** and downwardly for sufficient length to terminate above a bottom of the container assembly **12**. The dip tube **22** is desirably shaped to function as a baffle in the mixing container **12**, for example, with blades **64** extending laterally on either side thereof. The dip tube **22** preferably terminates at cap **66** provided with radially spaced slots **68** to minimize mixing between the contents of the container assembly **12** and countersolvent inside the dip tube **22**. If desired, thermocouple **70** can be affixed to the dip tube **22**, preferably on one of the blades **64**.

The dump mechanism **18** mounts adjacent the container assembly **12** for adding the oxidant particles thereto by remote actuation. As shown in FIG. **9**, the dump mechanism **18** includes receptacle assembly **70** and actuation lever **72**. The receptacle assembly **70** includes chute **74** affixed on one side to mounting plate **76** and spaced therefrom, and spring-biased mounting pins **78** which pass through respective bores (not shown) formed in the mounting plate and extend from an opposite side of the mounting plate **76** for attachment to the partition **26**. The receptacle assembly **70** is detachable from the chassis assembly **10** and actuation lever **72** for charging with oxidant particles, for example. While detached, a retaining clip **81** is used to hold a lower gate **80** in a closed position as seen in FIG. **11**. The lower gate **80** is hingedly connected at **79** to a lower end of the mounting plate **76** for selectively opening and closing a bottom of the chute **74**. The receptacle assembly **70** is removably attached to the partition **26** by means of the mounting pins **78** and keeper **83**. The keeper **83** is engaged in transverse bore **85** formed near an end of the mounting pins **78** between the mounting plate **76** and chute **74** (see FIGS. **10** and **11**). The gate **80** has a lateral pin **82** and clip **84** rotatably secured thereto for removable attachment to the actuation lever **72**.

The actuation lever **72** includes a cylinder **86** housing a pneumatically operable piston (not shown) connected to a shaft **88**. The cylinder **86** has a proximal end rotatably secured to the partition **26** via bracket **90**. The shaft **88** has distal end **92** with a transverse bore **85** (see FIG. **9A**) for slideably and rotatably receiving lateral pin **82**. The distal end **92** has a profile adapted to be received in the clip **84**.

As seen in FIG. **2A**, the countersolvent supply system **20** is mounted on the reverse side of the partition **26**. As shown in FIG. **12**, the countersolvent supply system **20** includes a tank **96** connected to a cross **98**. One port in the cross **98** is available for re-supplying countersolvent to the tank **96**. A line **100** supplies nitrogen or other inert gas from pressure regulator **101** to the top of the tank **96** at cross **98**. A sightglass **102** or other level indicator, is provided by connection at upper and lower ends of the tank **96**, for example, via cross **98** and tee **104**.

Countersolvent is supplied to the dip tube **22** from tank **96**, through tee **104**, line **106**, hand valve **108**, solenoid valve **110**, gravity leg **112** and decant/supply line **114**. The pressure regulator **101** maintains a uniform pressure in the tank **96**. Hand valve **108** has an adjustable orifice to establish a maximum countersolvent flow rate. The solenoid valve **110** is capable of continuous operation to supply the countersolvent at the maximum flow rate limited by the setting of the hand valve **108**, and can also be pulsed at different duty cycles to deliver countersolvent at a lower, precisely con-

trolled flow rate. A suitable solenoid valve **110** is commercially available, for example, a ½-inch Marrotta solenoid valve.

The gravity leg **112** is connected to a decant valve **116** positioned at a low point relative to the bottom of the dip tube **22** to establish a siphon from the container assembly **12** into waste line **118**. The decant/supply line **114** extends upwardly from the gravity leg **112** adjacent the decant valve **116** and passes through the partition **26** at fitting **120** to connect to the dip tube **22** on the opposite side thereof. During countersolvent delivery, the decant valve **116** is closed. The valve **116** is opened pneumatically when it is desired to decant liquid from the container assembly **12**.

With reference to FIG. **13**, some examples of alternate countersolvent supply and flow metering embodiments are schematically indicated. In the apparatus just described for the pressure method, a regulated pressure source **N** pads a countersolvent tank **T** equipped with a fill port **P**. In an example of a pump method as one example of an alternate embodiment, a pump **G** provides countersolvent from tank **T'** equipped with fill port **P'** at a constant pressure established by back relief valve **V1** which returns excess countersolvent to the tank **T'**.

Similarly, flow metering system **M** can use the single valve method described above, employing solenoid valve **110** in closed position (no flow), continuously open (maximum flow) or in a pulsed operation (low, metered flow). As described above, the hand valve **108** functions as an adjustable flow limiter. In an example of a two valve method as one example of an alternate flow metering embodiment, a parallel arrangement of continuously open or closed solenoid valves **S1** and **S2** can be used to establish high and low countersolvent flow paths. The flow rates can be established by the trim in valve **S1**, for example, and/or by using an orifice plate or hand valve **V2** to set fixed or adjustable flow rates. Similarly, a pump (not shown) could be used in place of decant valve **116**, particularly where the line **118** is not below the liquid level in the mixing container **12** as is need to establish a siphon.

As best seen in FIG. **4A** an inert gas-purged cabinet **120** can be mounted on the reverse side of the partition **26** to house the operating electronics, such as a control module (not shown) and any electrically operated valves such as solenoid valve **110**. The cabinet **120** can also house electrically operated pneumatic valve **122** and vent valve **124** (see FIG. **14**). An electric umbilical **126** can pass into the cabinet **120** via fitting **128** mounted in side wall **28**.

An example of a suitable nitrogen supply system is illustrated schematically in FIG. **14**. A high pressure nitrogen source **130**, for example, a 100 psig nitrogen tank, supplies nitrogen to lines **100,132** and **134**. Line **100** includes regulator **101** mentioned above, upstream pressure relief valve **136**, downstream pressure relief valve **138** and check valve **140**. Regulator **101** can be hand adjustable to provide the desired pressure to tank **96**, say on the order of 20 psig, for example. Relief valves **136** and **138** are designed to relieve overpressure conditions, for example, 120 psig and 25 psig, respectively, depending on system design parameters. The line **132** supplies nitrogen to actuator **142** for pneumatically operating decant valve **116**.

The line **134** supplies nitrogen to regulator **144** to establish a nitrogen pressure suitable for purging the cabinet **120**, for example, 50 psig. A downstream relief valve **145** protects against overpressure, for example, above 60 psig. A line **146** supplies nitrogen to orifice **148** to continuously purge the cabinet **120**, and to valve **122** for actuation of the cylinder

72 to open and close the lower gate 80 in the dump mechanism 18. Another orifice 150 supplies nitrogen to purge an enclosure 152 for the load cell 44.

The propellant blending system of FIGS. 1-14 can be operated remotely by operator and/or computer control. An exemplary control system schematic illustrated in FIG. 15 includes a control system housing 200 which can be located a remote distance from the apparatus of FIGS. 1-14 to provide operator safety. Electrical connection between the control system housing 200 is provided via the umbilical 128. The housing 200 is electrically connected to a ground 202 and is supplied with power, for example, 115 volts alternating current at input 204. The input 204 supplies power to an auxiliary power receptacle 206, motor driver/controller assembly 208 and power supplies 210, 212 and 214. The auxiliary power receptacle 206 can be mounted in a plate in the front or back of the housing 200 to use as an outlet for associated equipment, such as, for example, computer 226 and/or video monitor. Power supply 210 provides 24 volt direct current power to signal conditioners 216 and 218 which receive inputs from thermocouple 70 and load cell 44, respectively. Power supplies 212 and 214 supply 5 volt and 24 volt direct current power, respectively, to valve driver assembly 220. The motor driver/controller assembly 208, valve driver assembly 220, signal conditioners 216 and 218 and a key switch 222 are connected to computer 226 via junction block 224. The motor driver/controller assembly 208 can be selected between local and remote operational modes by means of selection switch 228 mounted on a front panel of the housing 200. In local operating mode, the speed of the motor 56 is controlled by the motor driver/controller assembly 208 via local speed controller 230 which is similarly mounted in a panel of the housing 200 adjacent to the selection switch 228. The valve driver assembly 220 provides output for operating dump mechanism actuator valve 122, dump mechanism vent valve 124, solenoid valve 110 and decant valve 116. Signal conditioners 216 and 218 provide input to the computer for the thermocouple 70 and load cell 44. The key switch 222 provides input to the computer 226 to indicate safe or armed status.

In operation of the propellant blending system of FIGS. 1-15, a solution of the binder and the fuel particles are placed in the container assembly 12. A premeasured quantity of oxidant particles is deposited in the chute 70 of dump mechanism 18. The tank 96 is filled with countersolvent as necessary and padded with nitrogen via line 100. The pivoting arm 36 is moved outwardly and the container assembly 12 is positioned to align the lugs 30A, 30B, 30C in the respective enlarged ends 29A, 29B, 29C. The container assembly 12 is then moved upwardly with the lugs 30A, 30B, 30C engaged in the slots 28A, 28B, 28C, the pivoting arm 36 moved in to place the support 40 below the container assembly 12, and the container 12 positioned thereon. The motor 56 is started to mix the contents of the container assembly 12. A countersolvent preload is added to the container assembly 12 by opening valve 110. Countersolvent passes through gravity leg 112, supply/decant line 114 and tube 22 into the container assembly 22, while maintaining agitation.

After the countersolvent preload is placed in the container assembly 12, the oxidant particles are dumped from the dump mechanism 18 into the container assembly 12, while maintaining agitation. Opening and closing the lower gate 80 several times helps to dislodge residual particles into the container assembly 12. The countersolvent is then metered into the container assembly 12 by opening or pulsing the metering valve 110 to supply countersolvent at a predeter-

mined rate through the gravity leg 112, decant/supply line 114 and dip tube 22. When sufficient countersolvent has been metered into the container assembly 12, agitation can be continued for a period of time to allow the particle aggregates to increase in size. Then, while maintaining agitation, the valve 110 is opened to supply excess countersolvent. While maintaining agitation, the contents of the container assembly 12 are stirred for a sufficient period of time to allow the aggregated particles to harden. The agitation is then stopped, and the particles allowed to settle to the bottom of the container assembly 22 as seen in FIG. 8.

Then the decant valve 116 is opened and the supernatant siphons from the container assembly 12 through the dip tube 22 and decant/supply line 114, out through gravity leg 112 and valve 116. When the liquid level in the container assembly 12 falls below the lower end of the dip tube 22 the siphon is broken by vapor. The valve 116 is then closed, and an additional countersolvent wash introduced via valve 110, gravity leg 112, decant/supply line 114 and dip tube 22. After checking the weight of the container assembly 12 via the load cell 44 to ascertain countersolvent addition, the motor 56 can be turned back on to mix the contents of the container assembly 12. The container assembly 12 is then removed, the propellant composition is screened in the countersolvent, and the recovered propellant particles dried in a vacuum oven.

A typical process flowchart of software for blending propellant compositions using the apparatus of FIGS. 1-15 is illustrated in FIG. 16. The operator manually loads the binder solution and fuel components into the container assembly, and the oxidizer components into the powder dump mechanism. The operator sets the key switch in the armed position, and starts the software. In the initial logic block 300, the computer algorithm verifies that all valves are in the off position. In block 302, the algorithm checks to ascertain that the motor controller is in the remote operating mode. In block 304, the key switch is monitored for status in the safe or armed position. The status of the key switch can be checked, for example, every 55 milliseconds to make that it remains in the armed position throughout the propellant blending process. If the key switch is turned to the safe position, the process is automatically terminated and text and audible warnings can be issued.

In block 306 the impeller is ramped to mixing speed, for example 1000 rpm. In block 308, the countersolvent preload is added. This is a predetermined quantity, translated into a period of time that the valve 110 is maintained in the continuously open position. In block 310, the agitation is continued for a period of time after the countersolvent preload is added to insure proper mixing before coacervation is initiated. A time period of 20 seconds is typical. In block 312, the impeller speed is adjusted, for example, increased from a typical 1000 rpm preload mixing speed to 1200 rpm. The speed of the motor 56 is then allowed to stabilize for a period of time, for example, 5 seconds, in block 314. Then, in block 316, the oxidant particles are added by actuating the dump mechanism 18, preferably several times to shake loose any oxidant particles which may cling to the surfaces of the chute 74 and lower gate 80. The mixture is then agitated for a period of time, in block 318, for example, about 30 seconds, to insure thorough dispersion of the oxidant particles in the binder solution.

In block 320, the countersolvent-solvent ratio is brought up to initiate coacervation. Using the input from the thermocouple 70, the solution temperature is measured. Based on the temperature measurement, the computer algorithm calculates the cloud point based on data specific for the

binder-solvent-countersolvent system. Based on the calculated cloud point, the countersolvent is added by continuously opening, or preferably pulsing, the valve 110. Once the countersolvent-solvent ratio of the cloud point is reached, the algorithm proceeds with block 344 to meter additional countersolvent into the container assembly 12 to a predetermined countersolvent-solvent ratio to precipitate a desired quantity of the binder from the solution. A countersolvent-solvent ratio of about 1.4 is typical in the heptane-acetone system with Viton B fluoropolymer in the preparation of ZPP propellant. Next, proceeding to block 324, the contents of the container assembly 12, are continuously mixed for a period of time to build aggregated particle size. A time period of 30 seconds is typical, although longer times can be used for obtaining larger particle aggregates. Then, in block 326, additional countersolvent is added, preferably by operating the valve 110 in a continuously open position, to achieve a predetermined countersolvent-solvent ratio, typically about 3.0 for the heptane-acetone system using Viton B fluoropolymer as the binder. The impeller speed can then be reduced in block 328 to minimize particle disaggregation which could result from excessive shear. In block 330, the mixing is continued for a period of time to allow the particles to finish hardening, typically on the order of 60 seconds. Proceeding next to block 332, the impeller is stopped and the particles are allowed to settle. The time required for settling depends on the specific components of the system, but a time period of about 10 seconds is typical. In block 334, the weight of the container measured by the load cell 44 is stored. The supernatant is siphoned next in block 336 by opening the decant valve 116. After allowing a sufficient period of time for the liquid to drain, in block 338, the load cell 44 reading of the weight of the container assembly 12 is taken and compared in block 340 with the weight stored in block 334. If the supernatant drained, additional countersolvent is added in block 342. If not, the software proceeds to block 344, terminating the process and issuing warnings.

After adding the countersolvent rinse in block 342, typically 1 liter, another load cell 44 reading is taken in block 346, and compared in block 348 with the reading stored in block 338. If the countersolvent added properly the software proceeds to block 350. If not, the software proceeds to termination/alarm block 344.

In block 350, the motor 56 is ramped to 1200 rpm, for example, for a relatively short time period, such as 10 seconds, to dislodge the settled particles, and then the speed is reduced to 1000 rpm, for example, for a longer period of time, e.g. 60 seconds, to thoroughly rinse the particles. Then in block 352, the motor 56 is stopped and the particles are again allowed to settle. Finally, the software terminates the process in block 354, turning all valves and outputs off, sounding an audible process end alarm, enforcing safe key operation and cycling the software for the next run. The operator can then remove the container assembly 12 for further processing of the propellant product as described above.

The amount of countersolvent preload, countersolvent-solvent ratio at the coacervation point and the countersolvent-solvent ratio to achieve suitable binder viscosity in logic block 322 (FIG. 16), is based on data specific for the particular binder, solvent, binder loading and countersolvent. Thus, the data must be obtained for the binder, solvent and countersolvent which will be used in the propellant blending process, at the binder concentration that will be used. The data are developed as a set of curves which plot the percentage of binder precipitated as a function of the

countersolvent-solvent volume ratio, over a range of temperatures likely to be observed during the blending process. A typical data matrix is illustrated graphically in FIG. 17 of the heptane-acetone system using Viton B fluoropolymer as the binder. The countersolvent preload is determined from this data to be about the most countersolvent which can be added without precipitating binder at the lowest temperature to be expected, taking into account ambient blending conditions as well as cooling resulting from any endothermic mixing of the solvent and countersolvent. For the heptane-acetone system of FIG. 17, the ratio is about 0.8.

From the data for the specific countersolvent-solvent-binder system, and empirical relationship between countersolvent-solvent ratio and coacervation temperature can be established as illustrated in FIG. 18. For use in the algorithm in logic block 320 of FIG. 16, it is useful to develop the relationship in the form an equation to calculate the countersolvent-solvent cloud point volume ratio as a function of the measured temperature.

For the countersolvent-solvent ratio used in logic block 322, it is desired to use the lowest ratio possible to precipitate about 50–90 percent of the binder, preferably 70–85 percent of the binder. If too much binder is precipitated too quickly, excessively large particles will form to an undesirable degree. If too little binder is precipitated, it is difficult to grow aggregated particle size properly.

EXAMPLE 1

The cloud point as a function of temperature and binder loading was determined empirically for Viton B fluoropolymer in acetone using heptane as the countersolvent. The data were obtained by adding heptane to a Viton B-acetone solution maintained in a temperature-controlled bath and recording the heptane-acetone volume ratio at the visually observed cloud point. The data are presented in Table 1.

TABLE 1

Viton B Loading (wt % in acetone)	Temperature (°F.)	Cloud Point (heptane/acetone ratio)
20 g/700 ml	28	0.77
	52	0.88
	68	0.94
	72	0.98
	75	1.00
	95	1.08

From these data, the cloud point was curve fit to the following equation:

$$R_{CP}=0.637+0.0047T$$

wherein R_{CP} is the heptane/acetone volume ratio at the cloud point, T is the temperature in °F. Data for this Viton B-heptane-acetone system are presented graphically in FIGS. 17 and 18. It is noted that these data were developed for Viton B having Mw of 500,000 and polydispersity (Mw/Mn) of 2.3, and would be different for different grades of Viton B depending on Mw, Mw/Mn, monomer composition, and other characteristics.

EXAMPLE 2

The apparatus of FIGS. 1–16 was used to prepare a simulated propellant. Tin powder (sp. gr.=7.31) was screened through a 325 mesh screen to simulate zirconium (sp. gr. 6.53). Sodium sulfate (sp. gr. 2.68) was screened through a 100 mesh screen to simulate potassium perchlo-

rate (sp. gr. 2.52). The binder was Viton B fluoropolymer (Mw=500,000; Mw/Mn=2.30), the solvent was acetone and the countersolvent was heptane as in Example 1.

The mixing container was a 6-inch ID vessel equipped with a one-inch vertical baffle and a baffle gap of ¼ inch. The impeller was a 3-inch diameter axial flow impeller with rounded blades mounted on a vertical shaft positioned about one inch above the bottom of the mixing container and about ½-inch horizontally from the wall of the mixing container opposite the baffle, i.e. about 1 inch off center.

A solution of 20 g of Viton B fluoropolymer in 700 ml of acetone was charged to the mixing container with 208 g of the tin powder. The motor was ramped to 800 rpm and 595 ml of heptane was added. Agitation at 800 rpm was maintained for 20 seconds, and then increased to 1200 rpm. The sodium sulfate (168 g) was added while maintaining the impeller at 1200 rpm. After 30 seconds, the temperature was measured to be 65° F. and the cloud point determined from the equation of Example 1 to be a heptane/acetone ratio of 0.94. Additional heptane (63 ml) was added to reach the cloud point. While maintaining the impeller at 1200 rpm, 140 ml more of heptane was pulsed into the mixing container over a 15 second time period by rapidly opening and closing a ½-inch Marrotta solenoid-operated valve, and the mixture stirred for 30 seconds. Then, 1302 ml of heptane were immediately added (90 ml/second) while maintaining the impeller at 1200 rpm. Stirring at 1200 rpm was continued for an additional 60 seconds after the heptane/acetone ratio was brought to 3.0.

The impeller was then stopped and the particles allowed to settle to the bottom of the mixing container. The siphon valve was opened to drain liquid until a vapor break occurred, corresponding to a liquid level about ½-inch above the settled particles. Removal of the liquid was confirmed by load cell readings. Then 1000 ml of heptane were added, the heptane addition confirmed by load cell readings, the container stirred at 1200 rpm for 60 seconds. The impeller was then turned off and the container removed.

The particles from the container were wet screened on a 20 mesh screen to remove oversized particles (about 5 g). The product was spread thinly on a tray and dried overnight in an oven at 140° F. The recovered particles were screened and had the particle size distribution shown in Table 2. The repetition of the above procedure obtained reproducible results.

TABLE 2

Screen Size (mesh)	Particle Size (microns)	Weight Percent Retained on Screen
30	595	0.8
40	420	1.3
50	297	2.1
60	250	11.3
80	177	68.6
100	149	15.3
200	74	0.5

EXAMPLE 3

The procedure of Examples 1 and 2 is followed to prepare a ZPP propellant for use in a NASA standard initiator (NSI). The NSI propellant is prepared with 52 weight percent zirconium, 42 weight percent potassium perchlorate, 5 weight percent Viton B fluoropolymer and 1 weight percent graphite. The zirconium specification is Mil-Z-399D, Type II, Class II with a maximum hafnium content of 3 percent

without ball milling to the final size. The potassium perchlorate is Mil-P-217, Grade A, Class 4 again with no ball milling to the final size. The Viton B fluoropolymer follows Dupont Sales Specification No. 14, 1985-02-06. The graphite is specified as Mil-G-155, Grade III, with a particle size less than 1 micron.

A solution of 20 g of Viton B fluoroelastomer in 700 ml of acetone is charged to the mixing container with 208 g of the zirconium powder and graphite. The impeller is brought to 1200 rpm and 595 ml of heptane preload are added. Agitation at 1200 rpm is maintained for 20 seconds and then the potassium perchlorate (168 g) is added while maintaining the impeller at 1200 rpm. After 30 seconds, the temperature is measured to be 65° and the cloud point is determined from the equation of Example 1 to be a heptane/acetone ratio of 0.94. Additional heptane (63 ml) is added to reach the cloud point. While maintaining the impeller at 1200 rpm, 322 ml more of heptane is pulsed into the mixing container over a 35 second time period by rapidly opening and closing a ½ inch Marrotta solenoid valve. The mixture is then stirred for 360 seconds. Then 1120 ml of heptane are immediately added (90 ml/second) while maintaining the impeller rate at 1200 rpm. Stirring at 1200 rpm is continued for an additional 60 seconds after the heptane/acetone ratio is brought to 3.0.

The impeller is then stopped and the particles allowed to settle to the bottom of the mix container. The siphon valve is opened to drain liquid until a vapor break occurs corresponding to a liquid level about ½ inch above the settled particles. Removal of the liquid is confirmed by load cell readings. Then 1000 ml of heptane are added, the heptane addition confirmed by load cell readings, the container stirred at 1200 rpm for 3 seconds, and then reduced to 1000 rpm for 60 seconds. The impeller is then turned off and the container removed.

The particles from the container are wet screened on 30 mesh screen to remove oversized particles (<1 gram). The product is spread thinly on a tray and dried overnight in an oven at 140° F. The ZPP product has a caloric content ranging from 1340 to 1450 calories per gram.

We claim:

1. Apparatus for manufacturing a solid propellant mixture of oxidant and fuel particles in a binder, comprising:

a mixing container;

a variable-speed impeller for agitating a mixture of binder, solvent and solid particles in the mixing container;

a countersolvent supply system for adding countersolvent to the mixing container;

a decanting line for removing supernatant liquid from the mixing container;

a control system for adjusting the speed of the impeller, adjusting the rate of countersolvent addition and actuating liquid removal from the mixing container, said control system including: (a) a countersolvent metering routine for effecting the steps of (1) adding the countersolvent to the mixing container with operation of the impeller up to about a coacervation point, (2) at about the coacervation point, matching the countersolvent addition rate and impeller speed to obtain a desired particle size distribution of the particles aggregated with the binder, and (3) thereafter adding excess countersolvent to the mixing container; and (b) a liquid removal routine for stopping the impeller, allowing particles to settle in the mixing container and actuating a valve in the decanting line to remove supernatant liquid from the mixing container.

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2. The apparatus of claim 1 wherein the countersolvent supply system includes a first and second countersolvent supply modes wherein the first mode has a low countersolvent flow rate relative to a high countersolvent flow rate of the second mode.

3. The apparatus of claim 2 wherein the countersolvent supply system includes a first flow path for delivering countersolvent to the mixing container at the relatively low flow rate of the first countersolvent supply mode, and a second countersolvent flow path in parallel with the first flow path for delivering countersolvent to the mixing container at the relatively high flow rate of the second countersolvent supply mode.

4. The apparatus of claim 2 wherein the countersolvent supply system includes a valve in a countersolvent flow path operable in a continuously open mode delivering countersolvent to the mixing container at the relatively high flow rate of the second countersolvent supply mode, and operable in a pulsed open and closed mode at a frequency selected to provide the relatively low flow rate of the first countersolvent supply mode.

5. The apparatus of claim 1 including a weight sensor for measuring changes in the weight of the mixing container.

6. The apparatus of claim 5 wherein the liquid removal routine includes a comparison of the mixing container weight before and after actuation of the valve to confirm removal of the supernatant liquid.

7. The apparatus of claim 1 wherein the control system includes a final countersolvent addition routine for adding

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additional countersolvent to the mixing container after execution of the liquid removal routine, comparing the mixing container weight before and after the additional countersolvent addition to confirm the countersolvent addition, and stirring the mixing container with the impeller.

8. The apparatus of claim 1 including a temperature sensor for measuring the temperature of the mixing container.

9. The apparatus of claim 8 wherein step (1) of the countersolvent metering routine includes adding a preload of countersolvent to within about 20 percent of the coacervation point, measuring the temperature of the mixing container, calculating the countersolvent-solvent ratio of the coacervation point at the measured temperature and adding additional countersolvent to the mixing container to make the calculated ratio of countersolvent to solvent.

10. The apparatus of claim 1 further comprising a dump mechanism remotely actuatable to add a supplemental charge of particles to the mixing container.

11. The apparatus of claim 10 wherein the supplemental charge comprises oxidant particles, the countersolvent supply system includes a tank including a charge of countersolvent, and further comprising a charge of fuel particles in a binder solution in the mixing container.

12. The apparatus of claim 11 wherein the fuel comprises zirconium, the oxidant comprises potassium perchlorate, and the binder comprises fluoroelastomer.

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