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(54) **Titre : COMPOSITIONS D'EMULSIONS EXPLOSIVES ET LEURS PROCEDES DE FABRICATION**
(54) **Title: EXPLOSIVE EMULSION COMPOSITIONS AND METHODS OF MAKING THE SAME**

(57) **Abrégé/Abstract:**

A detonator sensitive explosive emulsion composition includes an oxidizing phase including a supersaturated solution of ammonium nitrate and a fuel phase including sufficient emulsifying agent to permit dispersion of the oxidizing phase in the fuel phase. The detonator sensitive explosive emulsion composition further includes a crystallization temperature depressant consisting essentially of at least one of an amine and an amine nitrate.



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(54) Title: EXPLOSIVE EMULSION COMPOSITIONS AND METHODS OF MAKING THE SAME

(57) Abstract: A detonator sensitive explosive emulsion composition includes an oxidizing phase including a supersaturated solution of ammonium nitrate and a fuel phase including sufficient emulsifying agent to permit dispersion of the oxidizing phase in the fuel phase. The detonator sensitive explosive emulsion composition further includes a crystallization temperature depressant consisting essentially of at least one of an amine and an amine nitrate.

EXPLOSIVE EMULSION COMPOSITIONS AND METHODS OF MAKING THE SAME

Field of the Invention

5 [0001] The present disclosure is directed to detonator-sensitive explosive emulsion compositions comprising hexamine nitrate and/or one or more other amines or amine nitrates and to methods of making the same.

Background

[0002] Emulsion explosives are typically manufactured as a water-in-oil
10 emulsion at process temperatures between 40 and 100 °C. The water (oxidizer) phase typically consists of a supersaturated solution of ammonium nitrate (AN) and alkali metal nitrates, such as sodium nitrate, calcium nitrate, etc., or other crystallization temperature depressants at elevated temperatures. The oxidizer phase will crystallize (fudge) if cooled below the super-saturation temperature and
15 must be kept hot during processing. Depending on the composition of the oxidizer phase and the crystallization temperature depressant(s) used, the crystallization temperature of a typical oxidizer phase will be in the range of 30 to 100 °C.

[0003] The oil (fuel) phase typically consists of a mineral or vegetable oil, at least one surfactant and other viscosity modifiers, such as waxes, high molecular
20 weight oils etc. The oil phase is also kept hot during processing to prevent premature crystallization of the oxidizer phase. The emulsion is manufactured in a high shear mixer, whereby the oxidizer is broken into micron-sized droplets, coated by the oil phase. One unique property of water-in-oil emulsion explosives is that the oxidizer phase can be cooled to below its super-saturation temperature once the
25 emulsion is formed, without causing the oxidizer droplets to crystallize. However, excessive super-cooling will cause the oxidizer droplets to rapidly crystallize, causing the emulsion to become insensitive as an explosive. As used herein, references to the crystallization temperature of the emulsion refer to the crystallization temperature of the oxidizer phase, which refers to the temperature at
30 which crystallization would begin in a solution of ammonium nitrate and the crystallization temperature depressant.

[0004] The sensitivity of emulsion explosives to detonation by shock is governed by the water content of the emulsion. Detonator sensitive emulsions can be made by using only ammonium nitrate and water in the oxidizer phase, but the initial crystallization temperature (fudge point) of these solutions is so high that
5 adequate shelf life of the product can not be obtained. The problem is that the droplets of the oxidizer solution in the emulsion are super-cooled at room temperature, and if the degree of super-cooling is too high, the droplets will crystallize and the emulsion will become insensitive to the detonator. Sodium nitrate and sodium perchlorate have been used extensively to lower the fudge point
10 for detonator sensitive emulsions while keeping the water content low enough to maintain detonator sensitivity.

[0005] U.S. patents that describe the use of emulsions as explosives and the use of fudge point reducers include U.S. Patent No. 3,447,978 naming Harold F. Bluhm as inventor; and U.S. Patent Nos. 4,110,134; 4,138,281; 4,149,916; and
15 4,149,917 naming Charles G. Wade as inventor. Additionally, U.S. Patent No. 5,244,475 naming C. Mick Lownds and Steven C. Grow as inventors discloses the use of cross-linking agents in emulsion explosives.

[0006] Although adding sodium nitrate to the oxidizer solution lowers the crystallization temperature of the emulsion, sodium nitrate has also been observed
20 to actually desensitize the emulsion. Microballoons or gas bubbles have been used in explosives to act as "hot spots" during the detonation reaction, which are known to increase the sensitivities of emulsion explosives. Accordingly, in emulsions utilizing sodium nitrate as a crystallization temperature depressant, more microballoons or gas bubbles have to be added as a sensitizer to maintain
25 detonator sensitivity.

[0007] Emulsions using sodium nitrate for crystallization temperature depression can only be made at densities of less than 1.22 g/cc. Emulsions using sodium perchlorate to lower the fudge point can be made at densities of less than 1.32 g/cc. This gives a higher velocity of detonation, higher energy density in the
30 hole, and overall better performance. Therefore, sodium perchlorate has been the fudge point suppressor of choice for the best quality detonator sensitive emulsions.

[0008] In the United States, the use of sodium perchlorate in explosives has been banned in several states because of concerns with ground water contamination. Additionally, sodium perchlorate has become increasingly expensive and several countries are beginning to implement restrictions on
5 importing and shipping sodium perchlorate. Therefore, a less expensive and more convenient alternative needs to be found while preserving the advantages of sodium perchlorate (high velocity of detonation, high energy density, etc.).

[0009] Possible known alternative fudge point reducers are sodium nitrate, calcium nitrate, monomethylamine nitrate (MMAN) and hexamine nitrate solution
10 (HNS). As stated above, the problem with sodium nitrate is that it desensitizes the emulsion so more microballoons have to be used. The use of additional microballoons increases costs and decreases overall performance.

[0010] Monomethylamine nitrate is a very good fudge point reducer and it has been used extensively in cap sensitive water gel explosives, but not in emulsions.
15 One problem with monomethylamine nitrate is it is illegal to ship it in the United States. The problem is that when crystals of monomethylamine nitrate dry out, they become sensitive to detonation. Therefore, monomethylamine nitrate must be made on site if it is to be used in an explosive. Care must also be taken to not let small amounts dry out and form sensitive crystals. This requires careful testing of
20 piping systems for leaks and careful design so the monomethylamine nitrate does not sit and crystallize at any place in the system. In addition to the hazards involved in shipping, storing, and using the monomethylamine nitrate, it is also quite expensive to build a plant that can safely make monomethylamine nitrate. One reason for such expense is that anhydrous monomethylamine, one of the feed
25 components to any process for producing monomethylamine nitrate, is a flammable gas and must be kept under pressure to maintain it in the liquid state.

[0011] Hexamine nitrate is also a fudge point reducer and can be used to make explosives with good sensitivity and high velocity of detonation (VOD) values up to densities of at least 1.35 g/cc. However, hexamine nitrate has one primary
30 disadvantage as a fudge point reducer that has heretofore prevented its use in emulsion explosives. At high temperatures hexamine nitrate rapidly decomposes

into formaldehyde and ammonia, negating the crystallization temperature depressant properties of adding hexamine nitrate.

Summary

[0012] The present disclosure is directed to a detonator sensitive explosive emulsion composition comprising an oxidizing phase and a fuel phase. The oxidizing phase includes a supersaturated solution of ammonium nitrate in water. The fuel phase includes at least one oil and sufficient emulsifying agent to permit dispersion of the oxidizing phase in the fuel phase. In addition to the ammonium nitrate and water solution in the oxidizer phase and the oil and emulsifying agents in the fuel phase, the explosive emulsion composition may include one or more of wax(es), cross-linking agents, ammonium nitrate prill, aluminum, microballoons, gas bubbles, or other conventional components. Additionally, the explosive emulsion composition of the present disclosure includes at least one crystallization temperature depressant. The crystallization temperature depressant consists essentially of at least one of an amine and an amine nitrate.

[0013] The present disclosure is further directed to a method of producing a detonator sensitive explosive emulsion composition in a reactor. The reactor may include one or more mixers, blenders, coolers, heaters, tanks, or other process equipment as necessary to accomplish the method described herein. The explosive emulsion composition may be produced by adding an ammonium nitrate solution in water, an oil phase, and a crystallization temperature depressant to a reactor. The ammonium nitrate solution may be maintained at a temperature of about 90 °C or greater so as to avoid saturation or supersaturation of the solution and to prevent crystallization of the ammonium nitrate solution before reaching the reactor. The ammonium nitrate solution, the oil phase, and the crystallization temperature depressant are mixed in the reactor to form a water-in-oil emulsion. The reactor is maintained at a temperature of about 90 °C or more for less than about 24 hours after the crystallization temperature depressant is added to the reactor. More preferably the reactor is maintained at a temperature of about 90 °C or more for less than about 12 hours, and even more preferably for less than about 1 hour.

[0014] The above described method may be carried out in a variety of implementation configurations, including batch process and continuous process configurations. For example, the reactor may comprise a batch process reactor. The ammonium nitrate solution, the oil phase, and the crystallization temperature depressant may be added to the batch process reactor in any order and mixed to form the explosive emulsion composition. Similarly, the reactor may comprise a continuous process reactor, including at least an emulsion mixer adapted to mix the ammonium nitrate solution and the oil phase. In some implementations, it may be found to be advantageous to store the ammonium nitrate solution, the oil phase, and the crystallization temperature depressant separately prior to being combined in the emulsion mixer and/or prior to entering the emulsion mixer to form a feed stream to the emulsion mixer.

[0015] These and other features and advantages of the present description will become more fully apparent from the following description or may be learned by the practice of the methods as set forth hereinafter.

Brief Description of the Drawings

[0016] In order that the manner in which the above-recited and other features and advantages of the present disclosure are obtained will be readily understood, a more particular description of the present compositions and methods briefly described above will be rendered by reference to specific embodiments thereof which are illustrated in the appended drawings. Understanding that these drawings depict only typical embodiments of the methods and are not therefore to be considered to be limiting of its scope, the present methods and compositions will be described and explained with additional specificity and detail through the use of the accompanying drawings in which:

[0017] Fig. 1 is a schematic process diagram illustrating a method of producing the explosive emulsion compositions of the present disclosure;

[0018] Fig. 2 is a schematic flow diagram illustrating an exemplary batch process for producing explosive emulsion compositions; and

[0019] Fig. 3 is a schematic flow diagram illustrating an exemplary continuous process for producing explosive emulsion compositions.

Detailed Description

[0020] The presently preferred embodiments will be best understood by reference to the drawings. It will be readily understood that the components, as generally described and illustrated in the Figures herein, could be arranged and designed in a wide variety of different configurations. Thus, the following more detailed description of methods for producing explosive emulsion compositions, as represented in Figs. 1 through 3, is not intended to limit the scope of the present disclosure, but is merely representative of presently preferred embodiments.

[0021] Fig. 1 illustrates a schematic process flow chart of a method 10 of producing a detonator sensitive explosive emulsion composition. In its most basic description, the methods of producing explosive emulsions within the scope of the present disclosure include an oxidizer source 12, a fuel source 14, and a crystallization temperature depressant source 16, the contents of which are fed into a reactor 18 where they are mixed to form an emulsion 64. Additionally, one or more supplemental component sources 20 may provide additional components to the reactor 18 to modify one or more characteristics of the emulsion explosive. The emulsion 64 produced in the reactor 18 exits the reactor and is packaged, stored, or otherwise processed in the finish processor 22 for use as a detonator sensitive emulsion explosive composition. In some implementations, the process from introduction of the crystallization temperature depressant into the reactor to the packaging of the emulsion explosive composition may take less than about 24 hours, less than about 12 hours, or more preferably less than about 1 hour. In other implementations, the process may produce a stabilized emulsion explosive composition in less than about 24 hours, less than about 12 hours, or less than about 1 hour while the packaging step may occur later.

[0022] The oxidizer source 12 may be adapted to store or contain an oxidizing phase 24 to be fed to the reactor 18 via oxidizer feed stream 26. The configuration of the oxidizer source 12 may vary depending on the composition of the oxidizing phase 24 and the manner in which the oxidizing phase is fed to the reactor 18. For example, the oxidizer source 12 may be provided with a mixer 44. Additionally or alternatively, the oxidizer phase 24 may crystallize at ambient temperatures and

the oxidizer source 12 may include a heater and/or other temperature control elements to maintain the oxidizer phase 24 above its crystallization temperature. Similarly, the other sources, such as the fuel source 14, the crystallization temperature depressant source 16, and the supplemental component sources 20, may include heaters, mixers 44, and/or other components suitable for maintenance of the stored component in a suitable form and condition.

[0023] One exemplary oxidizer phase 24 includes an ammonium nitrate solution comprising about 87.5% ammonium nitrate and about 12.5% water. Other concentrations of ammonium nitrate solution may be used as the oxidizer phase. Similarly, the oxidizing phase 24 may include other components, which components preferably are not negatively affected by the conditions of the oxidizer source 12 and which components preferably do not negatively affect the oxidizer phase's ability to be fed to the reactor as a fluid stream. The exemplary 87.5/12.5 oxidizing phase has been found to have a crystallization temperature of about 85 °C. Accordingly, an oxidizer source 12 adapted to store an oxidizing phase 24 comprising the exemplary ammonium nitrate solution may include a heater assembly adapted to control the temperature of the oxidizing phase 24 to above 85 °C and preferably at about 95 °C. Ammonium nitrate and ammonium nitrate solutions are well known and their use in explosives is similarly well documented. As suggested, oxidizing phase 24 may include any suitable concentration of ammonium nitrate solution or solution made from ammonium nitrate mixed with other nitrate salts such as potassium nitrate, sodium nitrate, calcium nitrate, etc., and may be formed in any suitable manner.

[0024] The fuel source 14, similar to the oxidizer source 12, may be adapted to store and/or supply a fuel phase 28 to be fed to the reactor 18 via fuel feed stream 30. As is commonly understood, the fuel phase 28 for a water-in-oil explosive emulsion typically includes at least one mineral or vegetable oil 32. The fuel phase 28 may also contain one or more emulsifying agents 34 and/or viscosity modifiers 36. The ratio of oil 32 to emulsifying agents 34 and/or viscosity modifiers 36 may vary depending on the remainder of the components in the emulsion explosive and/or the intended usage of the emulsion explosives being

manufactured. Exemplary ratios will be provided below while other ratios may be implemented in accordance with the understanding developed from the present disclosure.

[0025] Continuing with the discussion of the schematic process flow diagram of Fig. 1, the crystallization temperature depressant source 16 is representative of the various process assemblies that may be used to supply crystallization temperature depressant(s) 38 to the reactor 18. As used herein, the crystallization temperature depressant 38 may also be referred to as a fudge point depressant 38. While a number of fudge point depressants have been used in prior emulsion explosives, the present fudge point depressants consist essentially of at least one of an amine solution and an amine nitrate solution. One exemplary fudge point depressant is hexamine nitrate solution. Other suitable amine solutions may include urea and mono-, di-, and tri-ethanolamine. Other suitable amine nitrate solutions may include urea nitrate and ethanolamine nitrates (e.g., mono-, di-, and tri-ethanolamine nitrates). The crystallization temperature depressant 38 may be fed to the reactor 18 by the depressant feed stream 40.

[0026] As illustrated in Fig. 1, the oxidizer feed stream 26, the fuel feed stream 30, and the depressant feed stream 40 each include a pump 42 in the stream. The pumps 42 are illustrative of the variety of equipment that may be included in the feed streams and/or in the component sources 12, 14, 16, 20 to facilitate the methods described herein.

[0027] Detonator sensitive emulsion explosives have been known for many years. As described above, the basic ingredients of ammonium nitrate and a fuel source have been supplemented over the years by a variety of other components that provide a variety of benefits to the emulsions. Supplemental component source 20 in Fig. 1 represents the numerous apparatus that may be used to introduce one or more supplemental components 50 to the reactor 18 via the supplemental feed stream(s) 48. Exemplary supplemental components 46 may include, ammonium nitrate in prill form (prill) 52, aluminum 54, and microballoons 56.

[0028] As will be seen in the discussion below of Figs. 2 and 3, the reactor 18 may be configured in a variety of suitable manners to incorporate a variety of process equipment 58. The schematic representation of Fig. 1 illustrates that the reactor 18 includes any suitable configuration that combines the oxidizer phase 22, the fuel phase 28, and the crystallization depressant 38 to produce a detonator sensitive emulsion explosive as described herein. Similarly, the finish processor 22 is illustrative and representative of the variety of process equipment that may be utilized to package, store, ship, etc. the finished emulsion composition.

[0029] As introduced above, the crystallization temperature depressant 38 may consist essentially of at least one of an amine solution and/or an amine nitrate solution. One exemplary amine nitrate solution is hexamine nitrate solution, which may be manufactured by combining hexamine and nitric acid in water. The hexamine nitrate solution may be manufactured in any concentration and a variety of suitable concentrations may be used within the scope of the present disclosure. An exemplary hexamine nitrate solution includes 61.4% hexamine nitrate in water.

[0030] A hexamine nitrate solution having 61.4% hexamine nitrate may be manufactured by adding water in a reactor, which may be the crystallization temperature depressant source 16 or another reactor that feeds into the crystallization temperature depressant source 16. Hexamine is then added to the water while stirring and cooling the reaction. Nitric acid may then be added slowly while continuing to stir and cool the reaction to maintain the temperature below about 50 °C. The reaction is then cooled to about 25 °C for storage and use, such as in the crystallization temperature depressant source 16. To provide a hexamine nitrate solution having 61.4% hexamine nitrate, the hexamine and the nitric acid may be added to the water to produce a final weight composition of 30.4 weight percent water, 43.9 weight percent hexamine, and 25.7 weight percent nitric acid (68%). The final hexamine nitrate solution (61.4%) at 25 °C may have a density of 1.240 ± 0.005 g/cc and a pH of from about 2.5 to about 7.0. Hexamine nitrate solutions of different concentrations may have different properties. For example, densities between about 1.1 g/cc and about 1.4 g/cc are within the scope of the present disclosure.

[0031] At high temperatures, hexamine nitrate solution tends to decompose into ammonia and formaldehyde gasses. In addition to the smell of ammonia and/or formaldehyde that may be present when the hexamine nitrate solution has begun to decompose, the decomposition can also be observed by a rise in the solution pH. Accordingly, the pH of the hexamine nitrate solution can be monitored in the crystallization temperature depressant source 16 to monitor the quality of the crystallization temperature depressant 38 being fed to the reactor 18. Crystallization temperature depressants of different compositions may have different temperatures at which decomposition begins and may result in different decomposition products, but similar characteristics and/or properties may be monitored for the different crystallization temperature depressants within the scope of the present disclosure. The exemplary hexamine nitrate solution has been observed to have a crystallization temperature between about 5 °C and about 10 °C; decomposition has been observed to begin at temperatures above about 30 °C. Therefore, the hexamine nitrate solution (61.4%) may be preferably stored at temperatures between about 10 °C and about 30 °C to avoid crystallization and decomposition. Accordingly, the crystallization temperature depressant source 16 may be adapted to maintain the depressant 38 within this temperature range.

[0032] Detonator sensitive emulsion explosives are used in a variety of applications and the composition of the emulsion explosives may vary to suit the desired applications. Exemplary variations of the emulsion explosive composition may include varying the presence and/or concentration of one or more of the supplemental components. For example, a suitable emulsion explosive composition may include a composition without supplemental components such as aluminum and prilled ammonium nitrate. Such a composition may be useful in applications to provide a lower energy, low cost explosive for use in all application diameters (e.g., 1" to 3.5" diameters). Exemplary uses of this "low energy" composition may include use as an ANFO booster and general blasting where high VOD is required but high total energy is not required. Additionally, a "high energy, small diameter" composition may be produced by adding 6.0% aluminum to the composition and varying some of the other concentrations accordingly. Still

additionally, an exemplary “high energy, large diameter” composition may be produced by adding 5.9% aluminum and 15% ammonium nitrate prill. Exemplary concentrations of the various components are shown in the following table for each of the exemplary compositions described above:

	Low Energy % w/w	High Energy, Small diameter % w/w	High Energy, Large Diameter % w/w	Exemplary Compositions % w/w
AN (in solution)	75.91	70.27	59.70	50-80
AN (prill)	0.0	0.0	15.00	0-30
Hexamine Nitrate	4.62	4.59	3.65	0.1-10.0
Emulsifier	1.76	2.00	1.39	1-3
Wax	2.00	2.00	1.58	1-3
Mineral Oil	0.16	0.0	0.16	0.0-5.0
Aluminum	0.0	6.00	6.00	0-10
Water	13.75	13.14	10.72	5-15
Microballoons	1.80	2.00	1.80	1-5
Total	100.00	100.00	100.00	100.00
Total Energy	749 cal/g	983 cal/g	1019 cal/g	600-1200 cal/g
Oxygen Balance	-0.34%	-6.84%	-2.77%	-10% - +1%
Density	1.25	1.25	1.25	1.0-1.4
Fudge Point	< 80 °C	< 80 °C	< 80 °C	< 80 °C

5

The concentrations shown in the preceding table and in the foregoing discussion are for illustration only. Other concentrations are within the scope of the present disclosure, such as may be appropriate to modify the explosive profile of the composition to meet the desired application. Suitable concentrations may include

compositions having concentrations within the ranges identified in the fourth column of the above table.

[0033] Crystallization temperature depressants 38 are primarily used to lower the crystallization temperature or fudge point of the oxidizer phase 24. Historically, the crystallization temperature depressants were stored together with the oxidizer phase, such as in solution therewith, and were fed to the emulsion reactor 18 together. However, the ammonium nitrate solution used in the oxidizing phase 24 is generally stored at elevated temperatures to avoid crystallization. For example, the exemplary ammonium nitrate solution (87.5%) has been observed to have a crystallization temperature of about 85 °C and is therefore generally stored at temperatures greater than about 90 °C. Due to the decomposition of the crystallization temperature depressants of the present disclosure, the methods of the present disclosure store the crystallization temperature depressant 38 separate from the oxidizer phase 24 until it is added to the reactor 18 to be incorporated into the emulsion explosive composition. Accordingly, the amount of time during which the crystallization temperature depressant is kept at an elevated temperature is reduced, thereby minimizing the decomposition of the fudge point depressant and preserving its functionality during the shelf life of the explosive emulsion composition.

[0034] Emulsion explosive compositions are generally evaluated for their explosive properties (e.g., total energy, velocity of detonation, detonation sensitivity, etc.) and also for their shelf life (e.g., flexibility of storage conditions and preservation of explosive properties over time). A particular composition may have ideal explosive properties but very poor shelf life characteristics rendering it virtually unsuitable for common use. As discussed above, emulsion explosive compositions have been observed to maintain their explosive properties at temperatures below the crystallization temperature of the ammonium nitrate solution once the emulsion has been formed. However, without fudge point depressants 38 in the emulsion composition, the compositions are supercooled to a greater degree under normal storage conditions (e.g., room temperature conditions) than compositions without fudge point depressants. This causes a

fairly short shelf life, due at least in part to the difference between the ammonium nitrate solution's fudge point (about 85 °C) and the storage temperature (about 25 °C).

[0035] Historically useful fudge point depressants, such as sodium perchlorate, have been observed to reduce the fudge point of the explosive emulsion to about 80 °C, which results in an extended shelf life under normal storage conditions. When the exemplary crystallization temperature depressant of the present disclosure, hexamine nitration solution (61.4%), is added to the emulsion explosive composition, the fudge point of the oxidizer phase is observed to be about 75 °C. Other crystallization temperature depressants within the scope of the present disclosure are believed to similarly reduce the fudge point of the oxidizer phase. Depending on the nature of the crystallization temperature depressant used, the amount of depressant 38 used relative to the remaining components may vary. Accordingly, the ratio of crystallization temperature depressant may vary in compositions within the scope of the present disclosure but will be sufficient to produce a crystallization temperature of less than about 80 °C.

[0036] Without being bound by theory, it is presently believed that the exemplary compositions described above will have a shelf life of one year or more without significantly reducing the explosive properties of the explosive emulsion composition. For example, compositions within the scope of the present disclosure may exhibit less than a 10% reduction in measured velocity of detonation after storage for one year. Additionally or alternatively, compositions according to the present disclosure may maintain greater than 90% of the total energy after storage for one year. For example, it has been observed that if the hexamine nitrate solution is left in an ammonium nitrate solution at temperatures greater than about 90 °C for more than 24 hours, the hexamine nitrate is almost completely decomposed thereby obviating any crystallization temperature depression that may have been intended by the addition of the hexamine nitrate solution. The explosives made from such solutions are no longer detonation sensitive and/or fail to propagate a detonation wave within a booster.

[0037] While crystallization temperature depressants within the scope of the present disclosure can be added to the explosive emulsion compositions without negatively impacting the explosive properties of the composition and while preserving and/or improving the shelf life properties, some amine solutions and amine nitrate solutions are known to add fuel value to the oxidizer phase 24. Emulsion explosives optimally have a zero oxygen balance so that the post-detonation products will have little or no excess carbon or oxygen. Therefore, the ratio of oxidizing components to fuel components is varied to attain the desired oxygen balance. Ammonium nitrate has a positive oxygen balance of +20% while the oils and waxes of the fuel phase generally have negative oxygen balances in the range of -300% to -350%. Accordingly, the ratio of ammonium nitrate to fuel phase is generally largely in favor of ammonium nitrate.

[0038] However, the amine solutions and amine nitrate solutions utilized in the present methods also have a negative oxygen balance, such as -48% for hexamine nitrate solutions, which requires adjustment to the ratio of oxidizer phase to fuel phase when compared to convention explosive emulsion compositions. However, if the ratio of fuel phase to oxidizer phase gets too low, the viscosity of the emulsion increases and may become so high that the product cannot be pumped or packaged conveniently. Hexamine nitrate has been used in water-based explosives in the past without confronting this viscosity problem because the continuous phase in water gels is the oxidizer phase and the ratio of oxidizer phase to fuel phase can be increased without increasing the viscosity of the water gel.

[0039] As seen in the table above showing illustrative concentrations of the various components in the present emulsions, the concentration of hexamine nitrate solution is quite low (3-5%) compared to the concentration of conventional fudge point depressants, such as sodium perchlorate, which can regularly approach 10%. While a variety of amine solutions and amine nitrate solutions are suitably within the scope of the present disclosure, the oxygen balance of the solutions must be considered in determining the suitability of the solution and in determining the concentration of the solution in the final emulsion explosive composition.

[0040] Detonator sensitive explosive emulsion compositions have traditionally included emulsifiers in the fuel phase to facilitate the dispersion of the oxidizing phase in the fuel phase. Additionally, the emulsifying agents were typically selected and added in sufficient concentrations to resist crystallization of the oxidizer phase in the emulsion in response to shock and/or shear events. It has been found that when hexamine nitrate solution is added as the crystallization temperature depressant, less emulsifying agent is required to maintain the resistance to crystallization under the same shock and/or shear events. It is presently believed that other amine solutions and/or amine nitrate solutions within the scope of the present disclosure will provide the same result, i.e., allowing the emulsion composition to include a lower concentration of emulsifying agents while maintaining good resistance to oxidizer phase crystallization under shock and/or shear events. In addition to the cost savings attributable to the reduced need for emulsifying agents, the decreased concentration of emulsifying agents also helps reduce the viscosity of the emulsion.

[0041] Without being bound by theory, it is presently believed that interactions between the emulsifiers and the amine groups on the fudge point depressants may be at least partially involved in the stabilization of the emulsion. For example, many emulsifying agents use amines as the molecular head groups, which may interact with the amines on the fudge point depressants. Additionally or alternatively, and also without being bound by theory, it is believed that the resistance to crystallization even with reduced concentrations of emulsifying agents may be at least partially attributable to the lower crystallization temperature attained by using the present fudge point depressants compared to the conventional depressants, such as sodium perchlorate. As discussed above, sodium perchlorate is generally known to lower the fudge point of explosive emulsion compositions to about 80 °C and the present fudge point depressants have been observed to lower the fudge point to at least as low as 75 °C.

[0042] As discussed at various locations above, the compositions and methods of the present disclosure may provide numerous advantages in the production of detonator sensitive emulsion explosive compositions. As just one

example, the use of hexamine nitrate is notably safer and cleaner compared to the use of sodium perchlorate, due to the concerns for groundwater contamination. Additionally or alternatively, one or more of the following advantages may be achieved through application of the principles of the present disclosure. Cost savings may be attained through the use of lower amounts of fudge point depressants, which may be required to maintain the desired oxygen balance and which may be possible due to the improved ability to lower the crystallization temperature of the emulsion composition. Moreover, at least some of the depressants within the scope of the present disclosure may be cheaper to produce compared to prior fudge point depressants. For example, hexamine nitrate solutions described herein are, at least at the present time, cheaper than sodium perchlorate solutions. Additionally or alternatively, as described above, the use of an amine or amine nitrate based solution may enable the composition to include a lower concentration of emulsifying agents. It has also been observed that in at least some of the implementations consistent with the present disclosure, fewer microballoons have been required, which further reduces the cost of producing the present emulsion explosive compositions.

[0043] In addition to the potential cost savings that may result from implementation of the present disclosure, the explosive properties of the composition are also modified by the principles taught herein. For example, the sensitivity to crystallization by shock and/or shear events may be reduced. Additionally or alternatively, the shelf life of the composition may be equal to or better than conventional compositions.

[0044] It has been observed that the total energy of the compositions including hexamine nitrate solutions as the fudge point depressant are slightly lower than the energies of similar compositions utilizing sodium perchlorate solutions. However, the lower energies are compensated for by the higher gas production of the emulsion compositions including hexamine nitrate solutions. Emulsions utilizing sodium perchlorate produce a variety of reaction products, some of which are not gaseous at the working temperatures of the explosion. In comparative tests between an explosive including sodium perchlorate and an

explosive including hexamine nitrate, the hexamine nitrate explosive produced 43.84 moles of gas per kilogram of explosive whereas the sodium perchlorate explosive produced only 40.97 moles of gas per kilogram of explosive. Comparing the same explosives, the sodium perchlorate explosive exhibited a total energy of 2,608.07 kJ/kg while the hexamine nitrate explosive exhibited a total energy of 2,362.10 kJ/kg. The roughly 9% lower total energy in the hexamine nitrate explosive is at least partially mitigated by the more than 7% greater total gas production. One manner in which the different levels of gas production makes a difference in the explosive properties is in the velocity of detonation measurements done of the different compositions. For example, a low energy, general purpose sodium perchlorate composition has been observed to have a total energy of 851 cal/g and velocities of detonation in the range of 5400 to 5600 m/s in a 2" diameter configuration. In comparison, a low energy, general purpose hexamine nitrate composition has been observed to have a total energy of 749 cal/g and velocities of detonation in the range of 5900 to 6100 m/s in a 2" diameter configuration. Accordingly, even in configurations where the total energy is lower, the explosive emulsion compositions of the present disclosure are able to provide a greater velocity of detonation, which is a significant advantage in some explosive applications, such as use as an ANFO booster.

[0045] As described above, the final emulsion explosive composition of the present disclosure includes an oxidizing phase, a fuel phase, and a crystallization temperature depressant. Additionally, the final composition may include one or more supplemental components common to explosive emulsions, such as aluminum, prill, microballoons, etc. The exemplary emulsion explosive described above included wax as a viscosity modifier. Additionally or alternatively, cross-linking agents may be used to obtain the desired rheology of the final composition. Considering the exemplary compositions provided above in the table, the compositions may be modified to incorporate cross-linking agents by replacing the wax with a suitable amount of mineral oil and/or vegetable oil and adding an appropriate amount of cross-linking agent. In some implementations, wax and cross-linking agents may be used together in the same compositions. In one

exemplary implementation of cross-linking agents to produce an emulsion explosive within the scope of the present disclosure, the wax may be replaced by mineral oil and about 0.2 w/w% of a maleanized polybutadiene may be added as the cross-linking agent. Other cross-linking agents may be used and the suitable concentrations may be varied as necessary. Additionally or alternatively, explosives within the scope of the present disclosure may omit wax and other viscosity modifiers entirely. For example, emulsion explosives according to the present disclosure may be configured as a bulk explosive wherein the viscosity modification is not required or desired.

10 **[0046]** While specific exemplary compositions have been described above and exemplary variations of the compositions have been described, the specific examples and descriptions provided herein are for illustration only and are not intended to limit the scope of the present disclosure or the claims presented below. For example, the formulas and weight percentages listed in the table above are
15 exemplary only. Any one or more of the components may have their respective concentrations increased or decreased to obtain different explosive properties, to modify the safety profiles, and/or to alter the cost structure of the compositions. As a most basic illustration of a modification that is within the scope of the present disclosure, the water content may be modified up or down depending on various
20 considerations.

[0047] In some implementations of the present disclosure, the components and their respective concentrations may be varied to accomplish one or more objectives, some of which may be balanced against others. For example, it may be desirable to produce an emulsion explosive having explosive properties
25 comparable or exceeding the explosive properties of sodium perchlorate-based emulsions but at a lower cost than the current products. Additionally or alternatively, without regard to costs, it may be desired to produce an emulsion explosive composition having a velocity of detonation at least as high as the currently available sodium perchlorate product. Additionally or alternatively, it may
30 be preferred to produce an explosive emulsion composition having an average shelf life of about one year or more. Still additionally or alternatively, the energy

and gap sensitivities may be at least as good as the currently available products. Other exemplary features of the present disclosure may be understood from the entirety of the present disclosure.

[0048] As discussed above, one problem that has previously prevented
5 hexamine nitrate solutions and other amine or amine nitrate solutions from being used as crystallization temperature depressants 38 has been the tendency of the hexamine nitrate to decompose under the temperature conditions of the oxidizer phase. The schematic method of Fig. 1 wherein the depressant 38 is maintained
10 separate from the oxidizer phase until the emulsion is ready to be produced and the process is completed through to cooling the emulsion within one day (preferably within about 12 hours, and more preferably within about 1 hour) illustrates one method of overcoming this problem; more specific methods are described in connection with Figs. 2 and 3.

[0049] As can be understood from the foregoing disclosure, the emulsion
15 explosive compositions of the present disclosure may be produced via any suitable method that combines an oxidizing phase, a fuel phase, and a crystallization temperature depressant in a manner that minimizes the amount of time during which the crystallization temperature depressant is subjected to elevated temperature conditions. Exemplary methods may include batch process methods
20 and continuous process methods. Referring back to Fig. 1, it can be seen that each of the principle starting agents (oxidizer phase 24, fuel phase 28, and crystallization temperature depressant 38) may be stored separately and maintained under conditions that are optimal for the respective components. For example, the crystallization temperature depressant 38 may be held at a low
25 temperature while the oxidizing phase 24 may be held at an elevated temperature. The reactor 18 may include any of a variety of process equipment 58 to facilitate the batchwise and/or continuous processes to produce the present explosive emulsion compositions. An illustrative schematic batch process 60 is illustrated in Fig. 2 while an illustrative schematic continuous process 70 is illustrated in Fig. 3.

30 **[0050]** Referring now to Fig. 2, the reactor 18 is illustrated as including a ribbon blender 62 for mixing the various components of the emulsion composition.

One or more additional or alternative suitable mixers and blenders may be used in the reactor 18 as well. For example, suitable blenders may include paddle blenders, screw blenders, scraped surface blenders, etc. Similar to Fig. 1, the batch process 60 of Fig. 2 includes an oxidizer source 12 providing an oxidizer phase 24, a fuel source 14 providing a fuel phase 28, and a crystallization temperature depressant source 16 providing a fudge point depressant 38. Additionally, Fig. 2 illustrates a plurality of supplement component sources providing one or more of the various supplemental components that may be incorporated into the final emulsion compositions. In the illustrated schematic, one such component source 20 provides a source of ammonium nitrate prill 52, while another provides a source of aluminum 54, and another provides a source of microballoons 56. Additional supplemental component sources 20 may provide one or more additional or alternative components as may be desired.

[0051] Fig. 2 illustrates that the various components are added to the ribbon blender 62 via separate feed streams and that the components are first combined in the ribbon blender 62. One or more of the components may be blended in an upstream mixer. Regardless of the precise configuration of the component sources and the reactor 18, the batch process 60 of Fig. 2 may be adapted to minimize the time during which the crystallization temperature depressant is held at an elevated temperature. In one exemplary configuration, the reactor may be maintained at a temperature of about 90 °C or more for less than about 24 hours after the crystallization temperature depressant is added to the reactor 18. In other implementations, the reactor temperature may be maintained above about 90 °C for less than about 12 hours or less than about 1 hour. As described earlier, the oxidizer phase 24 may include supersaturated ammonium nitrate solution in water and may be maintained at a temperature of 90 °C or more while in the oxidizer source 12. To avoid crystallization of the oxidizer phase, the reactor 18 may similarly be held at about 90 °C until the fudge point depressant 38 is added. Moreover, to facilitate the blending of the crystallization temperature depressant into the emulsion explosive composition, the crystallization temperature depressant

38 may be added at substantially the same time as the oxidizer phase 24 and/or the fuel phase 28, or at least in temporal proximity with the same.

[0052] The time required for the batch process 60 including a ribbon blender 62 to effectively mix the components to form the emulsion may depend on a number of factors, such as volume of the blender 62, quantity of materials being mixed, and characteristics of the emulsion composition, such as density, viscosity, concentration of emulsifying agents, etc. Once the reactor 18 has sufficiently blended the various components to form the desired emulsion composition, the contents of the reactor 18 may be moved to a finish processor 22 where the emulsion composition 64 is packaged and/or prepared for storage, shipment, etc.

[0053] The finish processor 22 may include cooling equipment to cool the emulsion composition to room temperature preparatory to the packaging and/or storage operations. The cooling equipment of the finish processor 22 may be adapted to quickly cool the emulsion composition to further limit the time during which the fudge point depressant is held at elevated temperatures. Depending on the amount of time the emulsion composition spends in the reactor 18 and the conditions therein, the finish processor 22 may be adapted to provide a variety of cooling profiles to minimize the time the fudge point depressant is at an elevated temperature. Additionally or alternatively, the cooling equipment may be configured to provide controlled cooling at the lower end of the cooling process so as to avoid and/or limit the super-cooling of the emulsion composition, thereby limiting the unintentional crystallization and desensitization of the emulsion composition.

[0054] While some or all of the cooling may occur in the finish processor 22, the emulsion composition may experience some cooling while still in the reactor 18. This cooling in the reactor 18 may occur due to an absence of applied heat while components at a lower temperature are being added to the reactor or may be caused through active cooling of the reactor. For example, the crystallization temperature depressant may be added at a temperature between about 10 °C and about 30 °C. In some exemplary implementations, the ribbon blender 62 may be adapted to be maintained at or above about 90 °C until the crystallization

temperature depressant 38 is added to the reactor, at which point the ribbon blender may be allowed to cool or induced to cool to at least about 75 °C.

[0055] Depending on the configuration of the equipment within the reactor 18 of the batch process 60, the reactor 18 may be maintained at a temperature of about 90 °C or more for less than about 8 hours after the crystallization temperature depressant is added. In other implementations, the temperature of the reactor 18 may be maintained at about 90 °C or more for less than about 2 hours or even less than about 1 hour after the crystallization temperature depressant is added. For example, active cooling may be applied upon introduction of the crystallization temperature depressant to lower the reactor temperature to about 75 °C as discussed above. Additionally or alternatively, the temperature of the reactor 18 may remain at or above 90 °C or may be uncontrolled and allowed to fluctuate according to the input temperatures of the components. Such an implementation may be acceptable in batch processes where the components of the emulsion composition are removed from the reactor 18 in less than twenty-four hours after the crystallization temperature depressant is added. For example, the ribbon blender 62 may be sufficiently efficient to complete the mixing of the emulsion composition 64 in 15 minutes, 30 minutes, 1 hour, 2 hours, 4 hours, 8 hours, or some other time sufficiently short to allow the emulsion composition to be cooled in the finish processor 22 without degrading the crystallization temperature depressant.

[0056] The batch process 60 of Fig. 2 may be operated with an oxidizer phase 24, a fuel phase 28, and a crystallization temperature depressant 38 as described above, in accordance with any one or more of the implementations or iterations described above. Similarly, the batch process 60 may be configured to produce an emulsion explosive composition 64 having one or more of the properties and features described above.

[0057] As indicated previously, Fig. 3 provides a schematic representation of a continuous process 70 for producing emulsion explosive compositions within the scope of the present disclosure. While not specifically illustrated in the figures, the present disclosure encompasses methods in which one or more steps are

continuous processes while other steps are batch processes. For example, the fuel source 14 may comprises a continuous process for producing the fuel phase wherein the continuous process includes mixing streams of oils, emulsifiers, and viscosity modifiers into a storage tank that is used to feed the method 10.

5 **[0058]** Fig. 3 illustrates that the schematic reactor 18 of Fig. 1 may include multiple pieces of process equipment 58 to facilitate the production of the emulsion explosive compositions 64. Fig. 3 further illustrates that regardless of the configuration of the reactor 18 and the configuration of the method as batch or continuous, the method includes an oxidizer phase 24 and associated oxidizer feed stream 26, a fuel phase 28 and associated fuel feed stream 30, and a crystallization temperature depressant 38 and associated depressant feed stream 40. As discussed above, the fuel phase 38 may include oils 32, emulsifying agents 34, and viscosity modifiers 36, among other possible components. As illustrated in Fig. 3, these components may be added to the fuel source 14 from their own sources, which may be separate sources to facilitate metering of the various components.

[0059] The reactor of Fig. 3 may include an emulsion mixer 72 adapted to combine at least the oxidizer phase and the fuel phase to produce an emulsion, which may be referred to as an intermediate emulsion 74 that is distinguished from the final explosive emulsion composition in that it does not yet include all of the intended components in the intended concentrations at the intended temperatures, etc. As illustrated in Fig. 3 by depressant feed stream 40, the emulsion mixer 72 may be adapted to incorporate the crystallization temperature depressant 38 into the intermediate emulsion 74. For example, and as illustrated, the oxidizer feed stream 26, the fuel feed stream 30, and the depressant feed stream 40 may all be initially mixed to form a single feed stream 76 to the emulsion mixer 72. Additionally or alternatively, one or more of the oxidizer phase 24, the fuel phase 28, and/or the fudge point depressant 38 may be added separate from the others and at any stage of the emulsion mixer 72. As one example, the crystallization temperature depressant 38 may be added to the emulsion mixer at an inlet mixer,

which may be inline with the feed stream containing the fuel phase and the oxidizer phase, or which may be offset therefrom.

[0060] The emulsion mixer 72 illustrated schematically in Fig. 3 represents the multitude of process equipment that may be implemented to produce an emulsion
5 from the fuel feed stream and the oxidizer feed stream. One or more alternative apparatus may be used alone or in combination to produce an intermediate emulsion that is then modified to produce the final emulsion composition.

[0061] Additionally or alternatively, some or all of the crystallization temperature depressant 38 may be added to the intermediate emulsion 74 after the
10 initial emulsion mixer 72. Fig. 3 illustrates that the reactor 18 may include a secondary mixer 78, which may be a paddle mixer or other suitable mixer, following the emulsion mixer 72 and receiving the intermediate emulsion 74. The secondary mixer 78 may be used to combine one or more supplemental components 50 into the intermediate emulsion 74. Exemplary supplemental
15 components 50 may include ammonium nitrate prill 52, aluminum 54, and/or microballoons 56, among other possible supplemental components. Additionally or alternatively, as illustrated by optional feed stream 80, some or all of the desired crystallization temperature depressant 38 may be added to the intermediate emulsion 74 in a secondary mixer.

20 **[0062]** While the exemplary continuous process 70 shown in Fig. 3 illustrates particular components entering particular process equipment 58, it should be understood that one or more components may be introduced at any suitable point in the reactor 18. For example, the optional feed stream 80 of the crystallization temperature depressant 38 may be configured to introduce the crystallization
25 temperature depressant 38 into the intermediate emulsion 74 before the intermediate emulsion enters the secondary mixer 78.

[0063] As discussed herein, the temperature of the crystallization temperature depressant 38, as well as the temperature of the other feed components, the intermediate compositions, and the final emulsion product may be monitored
30 and/or controlled to obtain the desired explosive properties of the final emulsion composition. Any one or more of the process equipment 58 that may constitute the

continuous process 70, such as the equipment 58 illustrated as comprising the reactor 18 of Fig. 3, may be adapted to apply active heating and/or cooling, to allow the ambient conditions to affect the reaction or mixing conditions, and/or to insulate the equipment from the ambient conditions. For example, the secondary mixer 78 may be adapted to actively cool the intermediate emulsion 74 so as to maintain the temperature of the secondary mixer, and thereby the temperature of the depressant 38, within an acceptable range, such as the temperature ranges discussed above.

[0064] As illustrated by output stream 82, the output 84 of the secondary mixer 78 may proceed directly to the finish processor 22 for packaging, shipping etc. Additionally or alternatively, the output from the secondary mixer 78 may proceed via an internal output stream 86 to an optional cooler 88. Cooler 88 may be adapted to cool the emulsion composition, which may be an intermediate emulsion or an emulsion already including all of its components, to maintain the temperature of the emulsion in the acceptable range so as to avoid crystallization of the emulsion and decomposition of the crystallization temperature depressant. As described above, any one or more of the process equipment 58 may include cooling functionality that may render the additional cooler 88 unnecessary. However, cooler 88 may be incorporated in lieu of adding cooling features to the other equipment or in addition to the cooling features of the other equipment. In one exemplary implementation, the secondary mixer 78 may have a temperature monitoring system (not shown) associated with the material about to be, or being, output from the mixer. In the event that the temperature monitoring system determines the temperature of the output 84 is acceptable, the output may be directed to output stream 82. In the event that the temperature monitoring system determines that the temperature is too high, the output 84 may be directed to the internal output stream for direction to the cooler 88. The cooler 88 may provide active cooling or may be configured to allow the output 84 to cool through exposure to ambient conditions.

[0065] In implementations that include a cooler 88 to effect the desired temperature reduction in the intermediate emulsion composition, Fig. 3 illustrates

that an additional secondary mixer 90 may be included in the reactor 18. For example, it may be desirable to delay the addition of the crystallization temperature depressant 38 until the emulsion is sufficiently cooled to avoid decomposition of the depressant. As illustrated in the optional configuration of Fig. 3, some or all of the crystallization temperature depressant 38 may be added to the emulsion as the final step in the reactor, such as being added to a secondary mixer 90 downstream of the cooler 88 or other apparatus adapted to reduce the temperature of the emulsion. The additional secondary mixer 90 may be of any suitable configuration, such as a paddle mixer or other available mixer.

10 [0066] Considering this illustrative optional configuration, some or all of the crystallization temperature depressant 38 may be directed via a bypass stream 92 to bypass the depressant feed stream 40 and to feed into the reactor process streams downstream of the cooler 88, such as being input into the additional secondary mixer 90, as illustrated in Fig. 3. The reactor process stream(s) entering the additional secondary mixer 90 may include the cooler stream 94 exiting the cooler, as shown in Fig. 3, or may come directly from the secondary mixer 78, such as when the secondary mixer 78 includes cooling functionality.

[0067] The various optional configurations of the continuous process 70 shown in Fig. 3 illustrates that the reactor 18 of the present disclosure may be configured in any suitable manner to produce an explosive emulsion composition wherein the crystallization temperature depressant 38 is held at an elevated temperature for a minimum amount of time. As described above, in the methods of the present disclosure the temperature of the reactor 18, or some component thereof, may preferably be maintained above about 90 °C for less than about 24 hours, less than about 12 hours, less than about 4 hours, and more preferably less than about 1 hour. As used herein, references to the temperature of the reactor 18 refer to the temperature of the reactor as a whole, an average temperature of the reactor, and/or the temperature of one or more components of the reactor. More particularly, such references refer to the temperature of the compositions in or

passing through the reactor and specifically to compositions that include crystallization temperature depressant.

[0068] It is believed that the disclosure set forth above encompasses multiple distinct methods and/or apparatus with independent utility. While each of these methods and apparatus has been disclosed in its preferred form, the specific embodiments thereof as disclosed and illustrated herein are not to be considered in a limiting sense as numerous variations are possible. The subject matter of the disclosures includes all novel and non-obvious combinations and subcombinations of the various elements, features, functions and/or properties disclosed herein.

10 The principles of the present disclosure may be embodied in other specific forms without departing from its structures, methods, or other essential characteristics as broadly described herein. The described embodiments are to be considered in all respects only as illustrative, and not restrictive. The scope of the disclosure is, therefore, not limited by the foregoing description or the following claims, and all

15 changes that come within the meaning and range of equivalency of the foregoing description and/or the following claims are to be embraced within its scope. Similarly, where the description and/or the claims recite "a" or "a first" element or the equivalent thereof, such description should be understood to include incorporation of one or more such elements, neither requiring nor excluding two or

20 more such elements.

[0069] It is believed that the following claims are directed to certain combinations and subcombinations that correspond to disclosed examples and that are believed to be novel and non-obvious. Other combinations and subcombinations of features, functions, elements and/or properties may be claimed

25 through amendment of the present claims or presentation of new claims in this or a related application. Such amended or new claims, whether they are directed to a different combination or directed to the same combination, whether different, broader, narrower or equal in scope to the original claims, are also regarded as included within the subject matter of the present disclosure.

CLAIMS

1. A detonator sensitive explosive emulsion composition comprising:
an oxidizing phase including a supersaturated solution of ammonium
nitrate;
5 a fuel phase including sufficient emulsifying agent to permit
dispersion of the oxidizing phase in the fuel phase; and
a crystallization temperature depressant consisting essentially of
hexamine nitrate in an amount of 0.1-10.0% w/w.
2. The explosive emulsion composition of claim 1, wherein the
10 hexamine nitrate added to the composition has a density between about 1.20 and
about 1.30 g/cc at about 25 °C.
3. The explosive emulsion composition of claim 1, wherein the explosive
emulsion composition has a crystallization temperature at which the emulsion
composition begins to crystallize, and wherein sufficient crystallization temperature
15 depressant is added to lower the crystallization temperature to below 80 °C.
4. The explosive emulsion composition of claim 1, further comprising a
crosslinking agent, and wherein the explosive emulsion has a density between
about 1.0 g/cc and about 1.5 g/cc and a crystallization temperature of less than 80
°C.
- 20 5. The explosive emulsion composition of claim 1, wherein the fuel
phase comprises sufficient emulsifying agents to maintain the dispersion of the
oxidizing phase in the fuel phase under shock/shear conditions.
6. The explosive emulsion composition of claim 1, wherein the
emulsifying agent in the fuel phase amounts to between about 1% w/w and about
25 3% w/w of the explosive emulsion.
7. The explosive emulsion composition of claim 1, wherein the oxidizing
phase comprises a supersaturated solution of ammonium nitrate in water; wherein
the fuel phase comprises mineral oil and sufficient emulsifying agent to permit
dispersion of the oxidizing phase in the fuel phase; and wherein the ammonium
30 nitrate constitutes between about 50 weight percent and about 80 weight percent

of the explosive emulsion composition, wherein the water constitutes between about 5 weight percent and about 15 weight percent of the explosive emulsion composition, wherein the mineral oil constitutes between about 0.01 and about 5.0 weight percent of the explosive emulsion composition, and wherein the
5 crystallization temperature depressant constitutes between about 0.1 weight percent and about 10 weight percent of the explosive emulsion composition.

8. The explosive emulsion composition of claim 1, wherein the composition is detonator sensitive after being stored for at least one year.

9. A method of producing a detonator sensitive explosive emulsion in a
10 reactor, the method comprising:

adding an ammonium nitrate solution in water to a reactor, wherein the ammonium nitrate solution is at a temperature of 90 °C or greater;

adding an oil phase to the reactor;

adding a crystallization temperature depressant to the reactor,
15 wherein said crystallization temperature depressant consists essentially of hexamine nitrate in an amount of 0.1-10.0% w/w; and

mixing the ammonium nitrate solution, the oil phase, and the crystallization temperature depressant; wherein the reactor is maintained at a temperature of 90 °C or more for less than about 8 hours after the
20 crystallization temperature depressant is added to the reactor.

10. The method of claim 9, wherein the reactor temperature is maintained at 90 °C or more for less than about 1 hours after the crystallization temperature depressant is added to the reactor.

11. The method of claim 9, wherein the reactor temperature is
25 maintained at 90 °C or more for less than about 30 minutes after the crystallization temperature depressant is added to the reactor.

12. The method of claim 9, wherein the hexamine nitrate solution comprises hexamine nitrate in a water solution having a density at about 25 °C of between about 1.2 and about 1.3 g/cc.

13. The method of claim 9, wherein the hexamine nitrate solution is added to the reactor at a temperature between about 10 °C and about 30 °C.

14. The method of claim 9, wherein the reactor comprises a batch process reactor.

5 15. The method of claim 14, and wherein the ammonium nitrate solution in water and the oil phase are mixed to form an emulsion prior to adding the crystallization temperature depressant.

16. The method of claim 15, wherein the reactor is maintained at a temperature of 90 °C or more before the crystallization temperature depressant is added, and wherein the temperature is maintained above 75 °C after the
10 crystallization temperature depressant is added.

17. The method of claim 9, wherein the reactor comprises a continuous process reactor including at least an emulsion mixer.

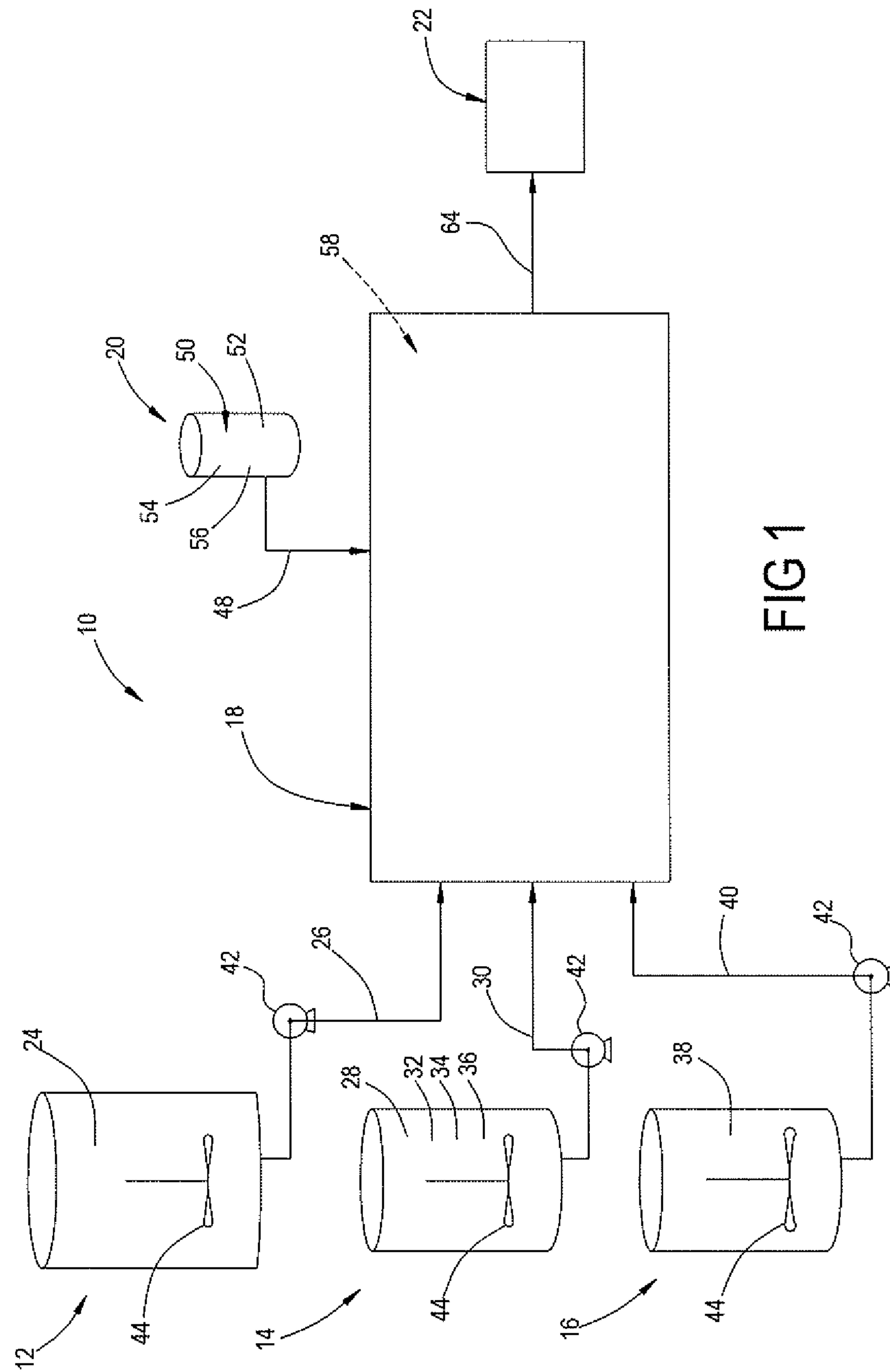
18. The method of claim 17, wherein the ammonium nitrate solution, the
15 oil phase, and the crystallization temperature depressant are stored separately and are combined to form a feed stream to the emulsion mixer.

19. The method of claim 18, wherein the emulsion mixer comprises an inlet mixer, and wherein the crystallization temperature depressant is added to the feed stream in the inlet mixer.

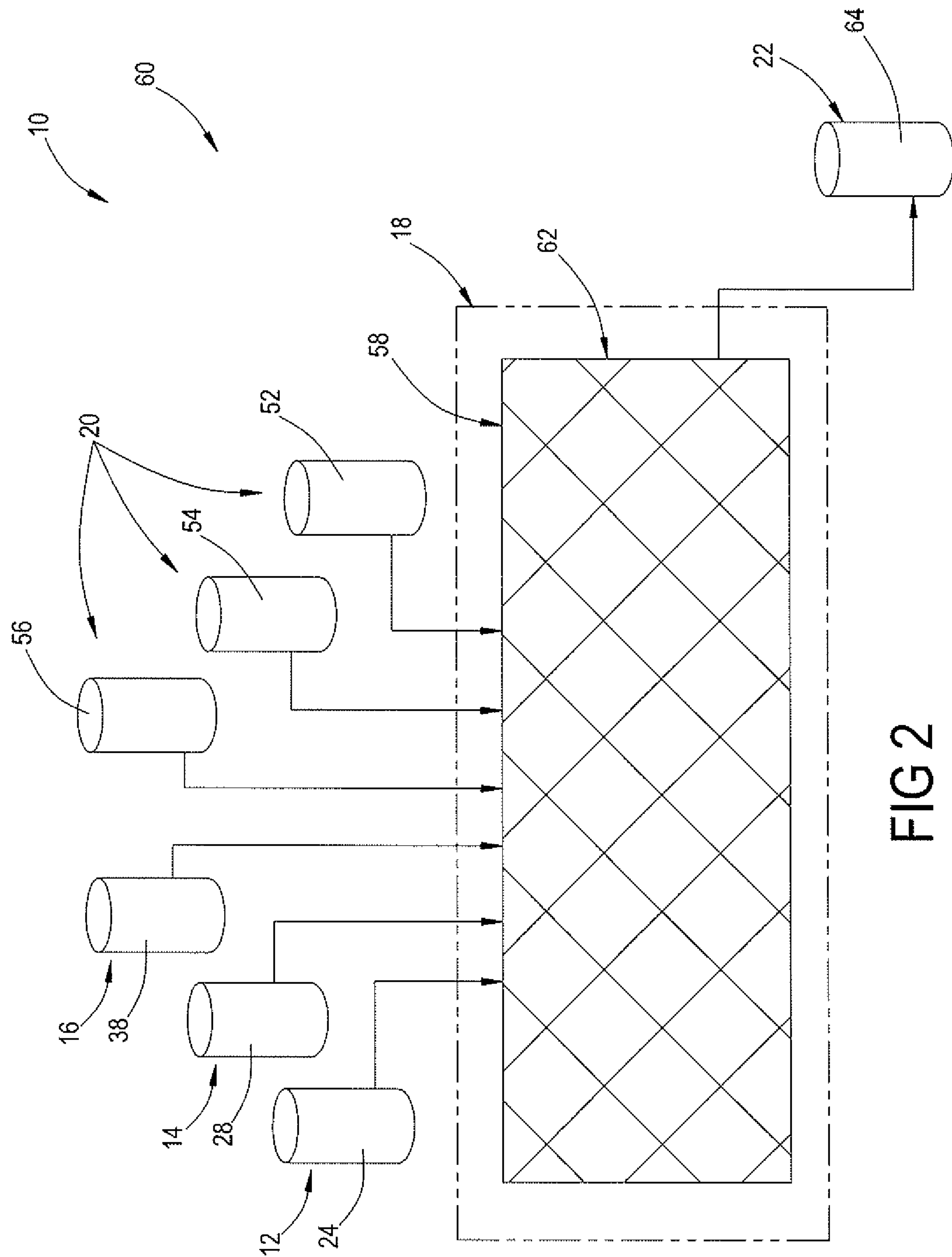
20 20. The method of claim 17, wherein the ammonium nitrate solution and the oil phase are combined in the emulsion mixer to form an intermediate emulsion, and wherein the crystallization temperature depressant is mixed with the intermediate emulsion in a secondary mixer downstream from the emulsion mixer.

21. The method of claim 20, wherein the continuous process reactor
25 further comprises an emulsion cooler downstream from the emulsion mixer, and wherein the crystallization temperature depressant is mixed with the intermediate emulsion downstream of the emulsion cooler.

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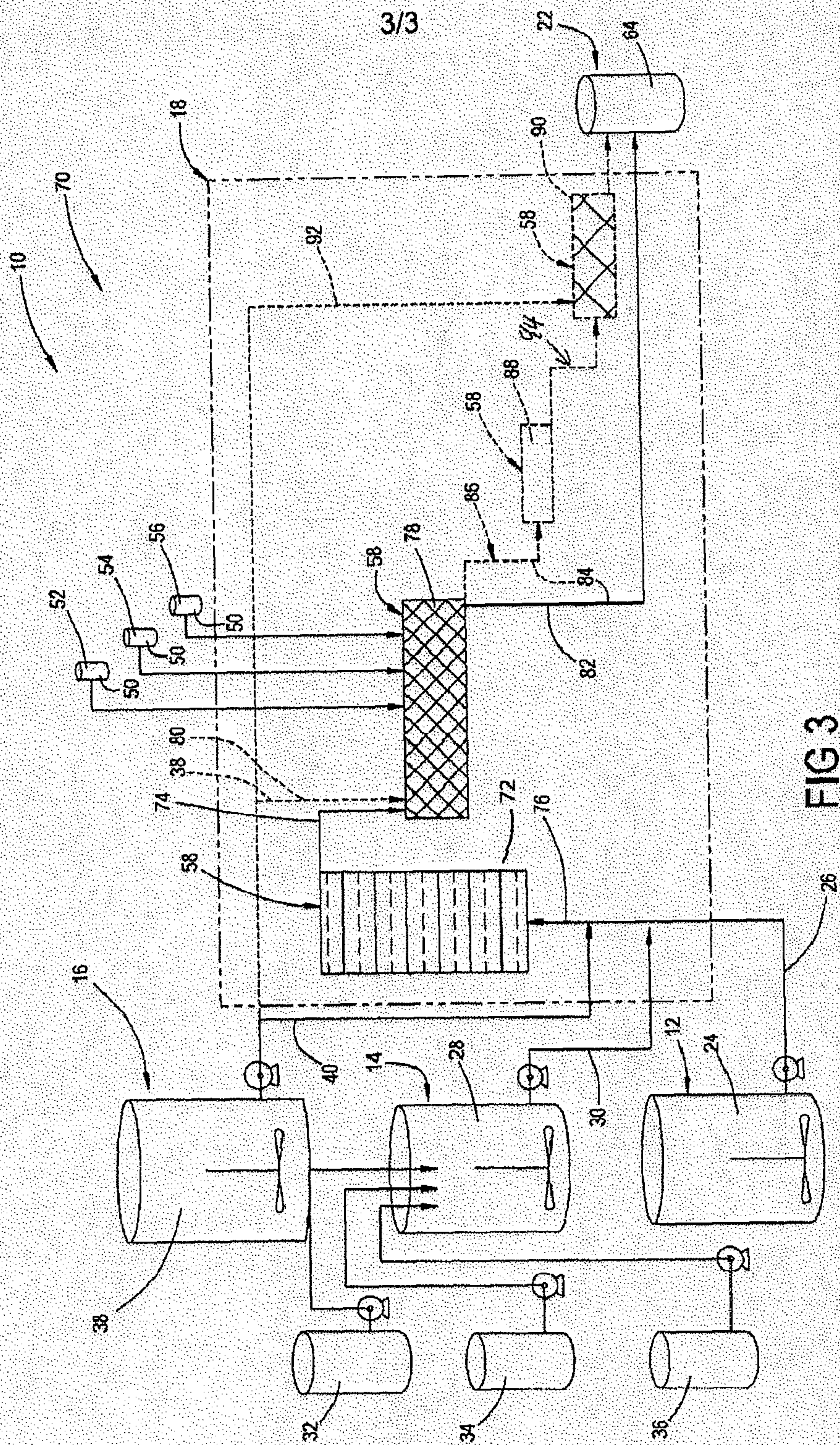


FIG 3