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3,361,601

GELLED AQUEOUS NITRIC ACID COMPOSITIONS

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27 Claims. (Cl. 149—19)

ABSTRACT OF THE DISCLOSURE

Aqueous nitric acid-based explosives gelled by the in situ polymerization of a mixture of mono- and polyethylenically unsaturated polymers soluble and stable in the system.

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a continuation-in-part of copending application Ser. No. 504,169, filed Oct. 23, 1965, now abandoned, which, in turn, is a continuation-in-part of copending application Ser. No. 486,223, filed Sept. 9, 1965, now abandoned.

DISCLOSURE

Liquid nitric acid finds use in the metallurgical, fertilizer, explosive, and general chemical process industries, where it serves principally in the preparation of inorganic nitrate salts or as a nitrating or oxidizing agent. However, use of the liquid acid as a chemical reactant or as an acidulating agent has always required special protection of both personnel and material, inasmuch as the inherent corrosiveness normally characteristic of a strong acid is accompanied in the case of nitric acid by particularly strong oxidizing capacity. These protective considerations also apply in the case of chemical propellants and explosives in which the oxidizing power of nitric acid is harnessed by reacting it under controlled conditions with one or more fuels.

The potential of liquid nitric acid as sole or principal oxidizing component in such high-energy compositions apparently was first clearly recognized by Dr. Hermann Sprengel in the early 1870's. In a paper in 1873 in the Journal of the Chemical Society (London), 26, 796–807, he noted that of all the then commonly available oxidizing agents, nitric acid contained the highest percentage of available oxygen. However, Sprengel also recognized the difficulties inherent in using the liquid acid as an oxidizing component for such charges. In British Patent 2642 of 1871, in which he initially proposed explosive compositions composed of liquid oxidizing agent, specifically nitric acid, in combination with one or more liquid or solid "combustible substances," i.e., fuels, a preferred method set forth for preparing such explosives was mixing of the oxidizer and fuel components immediately prior to use.

Since the time of sprengel's initial work on this type of charge, which often is referred to by his name, a number of attempts have been made to introduce modifications permitting easier and safer handling of such charges. For example, several variations directed particularly toward use of more economical and, in some cases, safer fuels and toward improvements in packaging and dispensing of the charges have been introduced, especially under the impetus of World Wars I and II, during which

charges of the Sprengel type were of increased interest for military use.

However, in spite of these modificaitons, explosives containing liquid nitric acid have never received widespread acceptance, either for military purposes or in the civil explosives market. A principal reason for this lack of acceptance is not difficult to ascertain. Liquid nitric acid is harmful to man, as well as to other animal and plant life, and injury or damage can result not only from contact with the liquid acid but also from exposure to the "fumes" (nitrogen oxides) that can evolve from the liquid acid under some conditions. Corrosiveness of the acid to many materials of construction likewise has been a problem, at least until relatively recently, in that the imperative for reliably leak-free storage, mixing and transfer facilities has often been associated with excesses in weight and in costs of making and using such equipment.

A less immediately obvious, but no less significant, disadvantage of some of the explosives containing liquid nitric acid is their sensitivity to detonation by impact, or high "shock sensitivity." Even when carefully prepared to avoid highly incompatible components and excessive heats of mixing, certain explosives of this type also have been known to "fume off" during formulation. Following Sprengel's procedure of mixing the liquid acid and fuel at the time and site of use, including mixing in the blast hole in the case of use of the charges as blasting explosives, can minimize the more serious consequences of these problems but simultaneously may generate new ones. For example, in loading of the charges into blast holes containing appreciable amounts of water, sealing or packaging material that is watertight and will remain so, even after several days' or weeks' exposure, is generally necessary. Otherwise, ingress of water can lead not only to desensitization so that the charges cannot be detonated, but also to decomposition reactions associated with the high heat of dilution of nitric acid in water. Even in so-called "dry holes," losses of liquid components through subterranean fissures or simmilar faults and reaction of the nitric acid with some minerals, e.g., carbonate-containing formations, can create problems.

Since maintenance of the liquid nitric acid and the fuel components in separated state until the time of use has not proved entirely satisfactory, either in terms of equipment and packaging requirements or in terms of the results achieved, other methods directed particularly toward immobilizing and/or dessensitizing the nitric acid-containing axplosives have been tried. For example, certain mineral substances of high absorptive capacity, such as kieselguhr and other diatomaceous earths, clays of various types and, more recently, colloidal silicas, have been proposed for use in nitric acid-containing explosives. These materials tend to thicken and immobilize the liquid explosives, or their liquid constituents, can in some cases impart a desirable reduction in sensitivity to detonation by impact, and may also help to provide at least temporary homogeneity in charges composed of nonmiscible components. However, such additives are inert, or substantially so, with respect to contributing to the total power of an explosive and hence are less than ideal constituents. Also they do not yield cohesive compositions of a wide range of consistencies.

More recently, a number of high-molecular-weight organic compounds, particularly certain linear polymers of

the vinyl type, have been found to swell in explosives containing liquid nitric acid and hence to impart a "thickening" effect. Unlike the inorganic modifiers referred to above, such organic thickeners do contribute to total explosive strength and power. Like the inorganic agents, they also can aid in providing homogeneity in compositions prepared from immiscible components, especially in the as-made state. However, neither of these types of additives is inherently capable of giving products of high viscosity, cohesiveness or flexibility. Water resistance, a desirable characteristic especially in explosives to be used in wet, or potentially wet, locations, also is not markedly improved by their use. Furthermore, what thickening and stabilizing action is initially imparted by the linear polymer additives often is lost, in whole or in part, inasmuch as certain of these additives tend to undergo degradation in the presence of nitric acid.

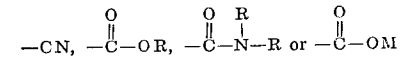
This invention provides a simple and effective means for obtaining modified aqueous nitric acid which is easier and safer to handle than that known heretofore and which has controlled free acidity and excellent stability. These and other properties of the improved nitric acid of this invention make the products of this invention particularly suitable as propellants, etching compositions, in chemical syntheses, as an acidifying agent in mineralogical processes, and in other uses where aqueous nitric acid is now employed. In addition, physical properties such as cohesiveness, controlled flexibility and consistency and the ability to maintain dispersion of solids therein as well as their explosive properties make compositions of this invention, particularly those containing conventional fuels, sensitizers, etc., outstanding and low cost explosives adaptable, for example, for formulation in fixed plant facilities as well as mobile and other on-site equipment.

The improvement of this invention comprises copolymerizing, in aqueous nitric acid of about from 5 to 99%, and preferably 30 to 98% strength, a mixture of mono- and polyethylenically unsaturated monomers soluble and stable in the system, said mixture comprising:

(a) About from 1 to 20%, and preferably 2 to 15%, by weight based on the aqueous nitric acid (i.e., the total weight of water and acid) of monomer selected from at least one of the group consisting of (1) monomers having the formula:



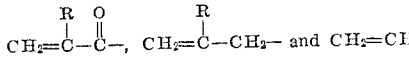
where X is



M is alkali or alkaline earth metal or an ammonium group and the R's are the same or different and each independently selected from the group consisting of hydrogen, lower alkyl, cycloalkyl, hydroxyalkyl, or cyanoalkyl radicals of 1 to 8, and preferably 1 to 4, carbon atoms, and (2) monovinyl pyridines and

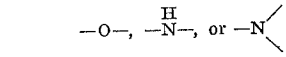
(b) About from 1 to 30%, and preferably 2 to 10%, by weight, based on (a), of monomer polymerizable therewith having at least two terminal unsaturated methylene ($CH_2=$) groups.

Preferably, the polyfunctional monomer (b) is selected from the group consisting of (1) monomers having the formula $[A]_nY$ and (2) divinyl benzenes, wherein A is selected from



the R's independently being selected from the group set forth above with regard to monomer component (a)

and the same or different from the particular R's in (a); n is 2 to 5, inclusive, and preferably 2 or 3; and Y is a bridging radical, preferably free of benzenoid unsaturation and of 3 to 20 atoms in addition to hydrogen, to which a plurality of the unsaturated moieties in (b) are bonded by oxygen or nitrogen atoms in Y; provided, however, that when the polyfunctional monomer component (b) consists essentially of at least one divinyl benzene, the monofunctional monomer (a) consists essentially of at least one monovinylpyridine. Preferably, the aforesaid bridging radical Y consists of carbon and hydrogen atoms alone or together with ether oxygen linked to the indicated unsaturated moieties through terminal



wherein —N< is a member of a heterocyclic ring, the shortest chain in Y adjoining each of said moieties and including said terminal atoms being about from 3 to 14 atoms long. The main requirement of Y is that it be stable in the system and not insolubilize (b). Compositions of this invention containing aqueous nitric acid of high strength, particularly those over 80% strength, preferably contain up to 60%, and preferably 5 to 30% by weight, based on the aqueous nitric acid, of dissolved salt of acid having an ionization constant in water of at least 10^{-6}. The preferred explosive compositions of this invention also usually contain fuels, sensitizers and other additives stable in the system including those conventionally used with Sprengel-type explosives. The aforementioned dissolved salts normally are dissolved in the aqueous nitric acid prior to polymerization. Other additives, including the additives for explosives, can be incorporated in the nitric acid prior to polymerization, or particularly in the case of additives of marginal stability or those having an inhibiting effect on polymerization, incorporated in the gel products after polymerization. However, in any case, the polymerization occurs in situ, that is, in the aqueous nitric acid component of the composition.

The expression "soluble in the nitric acid" and similar terms, as used herein, refer to components having appreciable solubility at ambient temperature (20–25° C.) in the particular strength of nitric acid being employed, i.e., a solubility of at least about 10% by weight, and preferably appreciably greater, e.g., 50 to 100%. Furthermore, the monoethylenically unsaturated monomer should not preferentially form, in aqueous nitric acid, homopolymers which are removed, e.g., by precipitation, from the aqueous nitric acid medium or agglomerate into flocculates or "lumps." Copolymerization forms a crosslinked structure which is a gel rather than a solid precipitate. This gelled structure swells in the aqueous nitric acid, holding the aqueous nitric acid, and is of substantially constant composition throughout. The gelled crosslinked structure contains a fairly low ratio of polymer solids to liquid phase, e.g., less than about 1:5, this ratio being roughly equal to the weight ratio of the monomers to the liquid phase, in contrast to precipitates or agglomerates in which there is a relatively high ratio of polymer solids to liquid phase.

Reference to stability in nitric acid unless otherwise indicated refers to the absence of significant degradation of the monomers, or their copolymerization products, in the particular strength of aqueous nitric acid involved. Since prolonged stability often is of special significance in the instant gelled compositions, stability in nitric acid unless otherwise specified refers particularly to the absence of appreciable degradation in copolymer-containing samples when they are subjected to an accelerated thermal stability test that involves heating of the material in question in nitric acid of the specified strength at a temperature of 50° C. (122° F.) for a period of at least 8 to 12 hours.

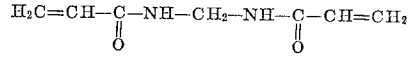
Strength as used with reference to nitric acid expresses in percent the relationship between the weight of 100% ("dry") nitric acid and the weight of nitric acid-plus-water in a particular acid. The aqueous nitric acid used in the compositions of this invention generally will have a strength of about from 5 to 99%. Most effective utilization of the gell compositions and their inherent properties is usually achieved, however, when the strength of the nitric acid employed is at least about 30%, particularly about from 40 to 98%, and these latter strength ranges will ordinarily be preferred. As will be described more fully hereinafter, certain specific strengths, or ranges of strength, within these broadly specified ranges can be especially suitable for particular applications of the gelled nitric acid compositions, for example, in the formulation of explosives and/or for use with particular copolymerization products.

Preferably, to effect gel formation at the lower concentrations of monomers and initiators and at ambient (room) temperature, the concentration of impurities such as metallic ions, e.g., of iron, chromium and nickel, which can be attributed to metal containers used to store the aqueous nitric acid, should not exceed about 5 p.p.m., since the presence of such impurities tends to inhibit polymerization. This is particularly desirable for acids of greater than about 75 to 80% strength.

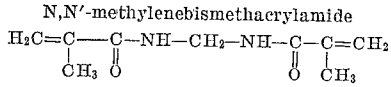
Examples of monoethylenically unsaturated monomers which can be used in this invention are vinyl pyridines such as 4-vinylpyridine and 2-methyl-5-vinylpyridine and acrylic monomers including nitriles such as acrylonitrile, methacrylonitrile, and α-butylacrylonitrile; acids such as acrylic acid, methacrylic acid, α-ethyl acrylic acid and α-propyl acrylic acid; esters such as methyl acrylate, methyl methacrylate, ethyl acrylate, n-butyl methacrylate and n-hexyl acrylate; amides such as acrylamide, methacrylamide, α-ethyl acrylamide, N-methyl acrylamide and N,N-dimethyl acrylamide; cycloalkyl substituted acrylics, e.g., cyclohexyl methacrylate; salts such as sodium or ammonium acrylate or alkyl ammonium acrylates; hydroxyalkyl acrylates, e.g., 2-hydroxyethyl acrylate or 2-hydroxypropyl acrylate; cyanoalkyl acrylics such as α-cyanoethyl-acrylonitrile; and mixtures of two or more of the aforementioned monomers. Acrylic and methacrylic acid and materials hydrolyzable thereto are particularly preferred because of the low cost and rapid polymerization in the process of this invention; of these acrylics, acrylic acid, acrylonitrile and acrylamide are of optimum efficiency. Although as previously indicated lower concentrations of monoethylenically unsaturated monomers can be used, usually the concentration ranges from 2 to 20% and, especially 3 to 15%.

Representative polyunsaturated monomers that can be used in this invention include one or more of:

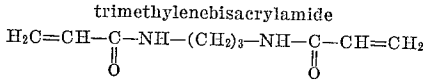
N,N′-methylenebisacrylamide



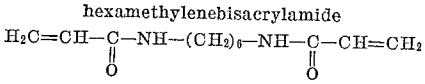
N,N′-methylenebismethacrylamide



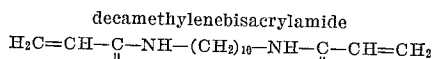
trimethylenebisacrylamide



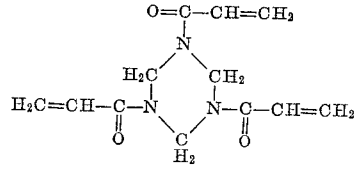
hexamethylenebisacrylamide



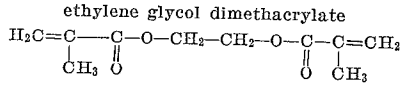
decamethylenebisacrylamide



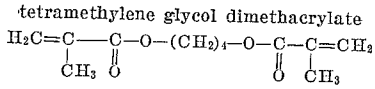
N,N′,N″-triacrylylhexahydro-s-triazine



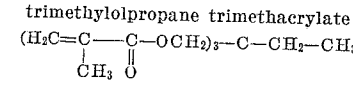
ethylene glycol dimethacrylate



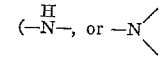
tetramethylene glycol dimethacrylate



trimethylolpropane trimethacrylate



Other polyfunctional monomers include acrylic and methacrylic acid esters, including mixed esters of polyols such as glycerine, sorbitol, mannitol, erythritol, pentaerythritol, diethylene glycol and triethylene glycol; cycloalkyl and hydroxyalkyl esters, e.g., ethylenebiscyclohexylacrylate and ethylenebishydroxyethylacrylate, and cyanoalkyl acrylics such as ethylenebiscyanoethylacrylate; polyallyl compounds such as diallyl ether, diallyl adipate, diallyl maleate, diallyl ether of pentaerythritol, diallyl amine, and N,N′-diallyladipamide; compounds with mixed groups such as allyl acrylate, allyl methacrylate, vinyl acrylate and vinyl methacrylate; and divinylbenzenes, particularly divinyl benzene per se. Of the aforementioned polyfunctional monomers, those having a bridging radical Y bearing terminal ether oxygen or amido



where —N< is part of a heterocyclic ring) nitrogen joined by an aliphatic chain of 1 or more alkylidene radicals



where R′ and R″ are selected from hydrogen, alkyl, cycloalkyl, aryl, or aralkyl radicals are preferred because of their optimum stability. Of these preferred polyfunctional monomers acrylic monomers including N,N′,N″-triacrylylhexahydro-s-triazine, trimethylolpropane trimethacrylate, ethylene glycol dimethacrylate, N,N′-methylenebismethacrylamide and, especially, N,N′-methylenebisacrylamide are particularly preferred. Alkylidenebisacrylamides wherein Y comprises a bifunctional alkylidene chain comprising 4 to 12, and usually 6 to 10, carbons with terminal amido functions are preferred polyfunctional monomers since gelled products produced therefrom have outstanding storage stability. Of these hexamethylenebisacrylamide and decamethylenebisacrylamide are particularly preferred. Divinylbenzenes are suitable for crosslinking the monovinyl pyridines.

Particularly when the gelled nitric acid of this invention is to be used as an explosive composition, the monomers employed for in situ copolymerization need not be highly purified. For example, acrylamides and methacrylamides obtained by the hydrolysis of the corresponding nitriles in the presence of concentrated mineral acid, e.g., sulfuric acid, can be used directly without purification. Also, if desired, at least a portion of the polyunsaturated monomer, e.g., methylenebisacrylamide, can be formed in the same crude hydrolysis mixture for example by adding an aldehyde such as formaldehyde thereto in proportion stoichiometrically necessary to yield the desired quantity of polyunsaturated monomer.

The choice of particular monomer components, as well as the concentrations of these components used to prepare the gelled compositions of the invention, both are influenced by the strength of the nitric acid and frequently also by the intended end-use of the resulting gelled composition. Generally speaking, the concentration of monomers increases with acid strength and desired gel consistency, while the mono and polyfunctional components are so selected that they have roughly similar polymerization rates under the reaction conditions. The aqueous nitric acid is converted from a liquid or water-like consistency to a gel characterized by the presence of an aqueous acid phase and a solid phase substantially uniformly distributed or dispersed therein. The gels are substantially homogeneous down to substantially colloidal dimensions and additionally resist finite shear forces. Thus, the copolymerization products form a continuous or semicontinuous matrix in the gelled compositions of the invention, at least a portion of the continuity in this matrix structure being provided by crosslinking of polymer chains by the aforementioned polyethylenically unsaturated monomer components which, owing to their polyfunctionality, are capable of reacting at two or more sites in the molecule. The proportions of liquid and solid phases have been found to be widely variable, so that a broad spectrum of product consistencies is readily obtainable, e.g., soft jellies, moderately stiff or very stiff gelatin-like masses that frequently are resilient, elastic, and even rigid shapable products. In addition, as will be shown more fully hereinafter, the consistency and other physical and mechanical characteristics of the gel products of this invention can be changed considerably through inclusion of a variety of other dissolved and/or dispersed components, in addition to the nitric acid and copolymer constituents. For satisfactory gel formation, the concentration of the aforedescribed monoethylenically unsaturated monomer or monomers used in forming the copolymerization products generally will constitute at least 1% and usually about 2% or more by weight of the aqueous nitric acid, although in a few cases somewhat lower concentrations can be effective. Higher minimum concentrations likewise can be desirable, depending particularly on the strength of the nitric acid, the particular monomer or monomers employed, and the presence or absence of additional dissolved or suspended components in the gelled compositions. On the other hand, the concentration of the monoethylenically unsaturated monomer(s) will usually not exceed about 20% by weight of the aqueous acid, since even where solubility considerations permit higher concentrations of these materials, the resulting gelled compositions are not materially improved thereby.

Compared to the monoethylenically unsaturated monomers, only relatively minor proportions of the above-described polyethylenically unsaturated monomer components have been found necessary to form gelled products possessing desirable consistencies and satisfactory stabilities. About from 1 to 30% by weight of the polyunsaturated monomer, with reference to the monoethylenically unsaturated component or components, will usually be used, although again the exact concentration will be influenced not only by the factors previously enumerated as affecting the amounts of monoethylenically unsaturated monomers used but also by the particular polyethylenically unsaturated monomer chosen. In general, the polyunsaturated monomers containing the carboxamido groups

$$(=N-\overset{\overset{O}{\|}}{C}-)$$

tend to be more effective at the lower concentrations of the specified range than do those containing the carboxylic ester groups

$$(-O-\overset{\overset{O}{\|}}{C}-)$$

The particular polyfunctional monomer used depends to some extent on the monofunctional monomer used. The polyfunctional monomer should polymerize sufficiently rapidly with respect to the monofunctional monomer so that, e.g., homopolymerization of the monofunctional monomer does not run substantially to completion before copolymerization begins. Thus, for example, if a vinyl pyridine is used, the polyfunctional monomer can be a divinylbenzene, while the aforementioned monomers of formula $[A]_nY$ can be used with a much wider spectrum of monofunctional monomers including both acrylics and vinyl pyridines.

At high acid strengths, particularly above 80%, it also can be desirable to have a dissolved salt present in the aqueous nitric acid used to form the gelled compositions of this invention. The addition of dissolved salt can also be desirable at acid strengths less than about 80% with the monofunctional nitrile monomers. To provide the necessary solubility in the nitric acid, such additive will ordinarily be chosen from salts of acids having a first ionization constant, measured in water at approximately 20° C., of not less than about 10^{-6}. As with the remaining components of the gelled compositions, the added salts should be stable in the aqueous acid, i.e., not undergo oxidation or reduction readily. They further should not have any deleterious effects on, i.e., not materially inhibit, the formation of the copolymerization products. The ammonium, alkali metal, and alkaline earth metal salts of acetic, nitric, sulfuric, chloric, perchloric and phosphoric acids, including both neutral and acidic salts in the case of the polyfunctional acids, generally satisfy these criteria and hence constitute a particularly suitable group of salts. Among these, the ammonium and potassium salts, e.g., NH_4NO_3, KNO_3, NH_4OAc, KOAc, $(NH_4)_2SO_4$, NH_4HSO_4, K_2SO_4, NH_4ClO_3, NH_4ClO_4, and K_2HPO_4, where "OAc" is acetate anion, have good solubility and effectiveness over a wide range of nitric acid strengths and usually are preferred.

The close interrelationship of the foregoing variables can be seen more clearly in terms of particular monomer combinations and specific strengths of nitric acid. For example, when acrylonitrile is used as the sole monoethylenically unsaturated monomer, it is particularly effective for gelling nitric acid having strengths of about from 50 to 80%. Preferred concentrations of the acrylonitrile under these conditions generally are about from 5 to 20% by weight of the aqueous acid, especially when employed in combination with about from 7 to 25% by weight, based on the acrylonitrile, of one of the previously described polyunsaturated monomers. However, superior gel formation, particularly in the upper portion of the specified nitric acid strength range, i.e., at strengths of about from 65 to 80%, can be achieved when the nitric acid contains one of the aforementioned dissolved salts, preferably in a concentration of about from 5 to 50% by weight. At the same time, the dissolved salt permits satisfactory gel formation from lower concentrations of the monomers, both mono- and polyunsaturated, than generally is possible in the absence of such salt.

On the other hand, when acrylamide is used as the sole monoethylenically unsaturated monomer, the strength of the nitric acid usually varies more widely, since this monomer is capable of giving preferred gels in nitric acid having strengths of about from 5 to 99%. This amide monomer generally will be employed in concentrations of about from 3 to 10% by weight of the aqueous nitric acid, together with about from 3 to 15% by weight, based on the acrylamide, of polyunsaturated monomer. Gel formation also is usually improved in these acrylamide-containing systems, especially at nitric acid strengths of about 80% or above, by the presence of dissolved salt in the nitric acid. Dissolved salt concentrations of about from 2 to 50% by weight of the nitric acid are usually employed. Again, the salt additive has a favorable ability

to lower the concentrations of monomers, both mono- and polyacrylic, effective for gel formation.

Acrylic acid, methacrylic acid, and esters of these two acids are all similar to acrylamide in terms of effective concentrations of the mono- and polyunsaturated monomers and also in terms of salt addition. Systems containing these latter monomers find particular use in gelling nitric acid having a strength of about from 50 to 99%.

Still further variations in component proportions and properties of the gelled products are possible through use of mixtures of at least two of the aforementioned monoethylenically unsaturated monomers. Acrylonitrile can be combined with acrylamide or acrylic acid, for example. In such mixtures, most effective utilization of the monomers and the gelled products and their properties generally is achieved when the acrylonitrile constitutes a maximum of about 80% by weight of the total monoethylenically unsaturated monomer mixture. Under these conditions, the nitric acid strength is about from 50 to 75%, the concentration of monoethylenically unsaturated monomer about from 4 to 15% by weight of the aqueous nitric acid, and the concentration of the polyunsaturated monomer component on the order of about from 5 to 15% by weight of the total monoethylenic monomers. Other combinations of monoethylenically unsaturated monomers found particularly effective under similar conditions in preparing the gelled nitric acid compositions of this invention include mixtures of acrylonitrile and methacrylic acid, mixtures of acrylamide and acrylic acid, mixtures of acrylamide and methacrylic acid, and mixtures of acrylic acid and methyl acrylate.

In addition to the aforementioned constituents, the reaction mixtures used in preparing the compositions of this invention also contain one or more promoters or initiators which are soluble at least to the extent of 0.1%, and preferably to substantially greater extent, in aqueous nitric acid and not substantially consumed or inactivated before polymerization, e.g., not consumed or inactivated after about 30 minutes at polymerization conditions. Promoters meeting the above criteria include sodium, potassium and ammonium salts of inorganic per acids such as persulfates, perborates and pervanadates; hydrogen peroxide, particularly in combination with ferrous ion; cobaltic ion (Co^{+3}) alone or in combination with hydrazine or persulfate; and organic peroxide and azo catalysts such as azobis(isobutylnitrile), α,α'-azobis(α,γ-dimethyl-γ-methoxyvaleronitrile, tertiary butyl hydrogen peroxide, methylvinyl etherhydrogen peroxide, and peracetic acid. Inorganic redox couples, combinations of reducing and oxidizing agents, are preferred. With some promoters such as the aforementioned organic azo and peroxide catalysts as well as with the cobaltic ion alone and the ferrous ion-hydrogen peroxide couple, it is preferable to use weaker acids particularly of less than 50% strength.

Redox systems that utilize a source of persulfate ion ($S_2O_8^{-2}$) as one component have been found especially suitable in these respects throughout the range of acid strengths. The persulfate ions, which are introduced into the nitric acid as a soluble persulfate salt, e.g., an ammonium or alkali metal salt, can be used alone with the nitric acid as a redox couple to promote the copolymerization reaction.

An added reducing agent can also be used in forming the polymerization catalyst or promoter system. Reducing agents found to be especially suitable in having the required solubility, activity and stability in nitric acid include certain nitrogen bases, especially hydrazine, hydroxylamine, and carbohydrazide. These reactants can be introduced as the free bases, as hydrates, or as soluble salts of inorganic or organic acids, preferably free of halogen. Among the mentioned reducing agents, hydrazine is especially effective and is preferred, particularly when used in combination with persulfate and copper ions. Optimum utilization of added reducing agent is generally realized in aqueous nitric acid of strengths up to about 85%, the reactants usually being less effective at higher acid strengths.

Generally higher rates of polymerization are achieved when the polymerization system also includes a minor amount of metal ion, usually transition metal ion. Group IB metal ions, especially silver and copper ions, are particularly effective for this purpose. These metal ions also are introduced as soluble inorganic or organic salts, e.g., as the nitrates, sulfates, or acetates. (Halogen-containing salts, especially those containing chlorine, should generally be avoided inasmuch as they tend to retard or inhibit the copolymerization reaction.) Other preferred persulfate couples are H_2O_2—$[S_2O_8]^{-2}$, Co^{+2}—$[S_2O_8]^{-2}$, and Fe^{+2}—$[S_2O_8]^{-2}$.

In general, the total amount of promoters varies somewhat with the particular promoter and monomers and increases, at least at low concentrations, with the desired speed of polymerization and concentration of monomer, but usually falls within the range of about from 0.1 to 30% based on the total weight of monomers to be polymerized. The optimum concentration of the preferred persulfate ions, based on total monomers, both mono- and polyethylenically unsaturated, can vary considerably, depending on the particular polymerization system, including the presence or absence of additional promoter components, but ordinarily will be about from 0.1 to 15 weight percent of the combined monomers. Even higher concentrations are without deleterious effect, but offer no advantages in terms of polymerization rates or product quality. In general, it is preferred to employ about from 0.5 to 10% by weight of persulfate ions, based on the total monomers.

Silver ion, when used as a promoter, generally is effective in ratios of about from 0.1/1 to 5/1, with reference to the weight of persulfate, and weight ratios of about from 0.3/1 to 3/1 are usually preferred. Copper ion in combination with hydrazine on the other hand, is most active as a polymerization promoter at much lower ratios, viz, about 0.005/1 to 0.5/1, based on persulfate ion, and preferably is employed in concentrations providing a copper-to-persulfate ion weight ratio of about from 0.01/1 to 0.3/1. Relatively slow polymerizations are achieved with silver ion as a promoter, compared to those when copper ion and hydrazine are used. Thus, considerable variation in rates of gelation can be obtained through choice of a particular metal ion as well as its concentration.

The added reducing agent, when used, will generally be present in a weight ratio, based on persulfate, of about from 0.01/1 to 2/1, and preferably from about 0.01/1 to 0.5/1.

Preparation of the gelled nitric acid compositions of this invention can be accomplished by simple mixing of the nitric acid, optionally containing dissolved salt, with the mono- and polyethylenically unsaturated monomers, followed by addition of the polymerization-promoting component or components. In a few cases, solution of the monomers in the nitric acid can be facilitated by first dissolving them in a small amount of water; such water is of course taken into consideration in determining the desired final acid strength. The mixing and polymerization steps ordinarily are conducted at ambient temperatures (20–25° C.), but temperatures down to the freezing point of the mixture can also be used without deleterious effects except for a lower rate of reaction. Temperatures above about 40 to 50° C., on the other hand, should ordinarily be avoided during the polymerizations, in that they tend to inhibit gelation even when the resulting gelled compositions, once formed, are capable of withstanding temperatures at or above this level. When preparing gelled compositions using low monomer concentrations, e.g., less than about 3% total monomer, the reaction mixture is preferably maintained at lower temperatures, e.g., at about 10–15° C.

The rate of polymerization and, in some instances, product consistency can also be affected by the presence of nitrogen oxides and oxygen, either in dissolved form or as

the gases, as well as by the presence of large amounts, in the monomers, of compounds conventionally used to inhibit free-radical polymerizations of the same. Compensation for these variations can be provided, when necessay, by increasing slightly the concentrations of the monomers and/or of the polymerization promoters. An alternative and generally more economical procedure, however, is to reduce the concentrations of these polymerization-retarding components prior to the polymerization. In the case of the nitrogen oxides and oxygen, this can be accomplished by sparging the nitric acid with an inert gas, e.g., nitrogen or carbon dioxide, and then preferably maintaining it under an inert gas atmosphere until the polymerization reaction is complete.

The rate of gelling and the viscosity of the gelled compositions of this invention can be varied according to the needs of a particular application. In general, the rate of gelling and the viscosity of the gel can be increased by increasing the strength of the acid, by increasing the percentage of monoethylenically unsaturated monomer in the system, by increasing the relative proportion of the polyethylenically unsaturated monomer used for a given quantity of the monoethylenically unsaturated monomer, and/or by increasing, within limits, the quantity of polymerization promoter, such as persulfate and/or hydrazine employed in the system. The addition of a dissolved salt, typically ammonium nitrate, to the system usually increases the viscosity of the final gelled products, and, as is discussed above, is usually preferred for use in gelling nitric acid of greater than about 80% strength.

The compositions of this invention have greater homogeneity, resistance to disintegration or leaching by water, and stability, i.e., resistance to degradation and settling out of components, than compositions which are merely thickened. This greater homogeneity, stability and water-resistance is particularly advantageous when the gelled nitric acid compositions, which can contain added fuels and sensitizers, are to be used as explosives particularly in wet locations, since disintegration and leaching of a composition by water, if such occurs, can lead to failures to detonate or to propagate a detonation throughout the length of an explosive column. If the explosive structure degrades, i.e., by virtue of disintegration of the gel structure, subsequent segregation of components, particularly undissolved (solid) fuels and sensitizers, as discussed hereinafter, can occur under the force of gravity, and the components in a borehole, whether in a container or cartridge, shucked therefrom, or simply pumped into a borehole will become so heterogeneous that complete failure of detonation or propagation of detonation through the entire length of the column of explosive charge will occur.

As indicated hereinbefore, the gelled nitric acid compositions can be employed for a variety of applications in which liquid aqueous nitric acid is ordinarily employed, e.g., as an oxidizing or nitrating agent in chemical synthesis, as an acidifying agent in mineralogical and other processes, in preparing nitrate salts, and in like operations. The gelled nitric acid compositions find particular merit in such applications when delayed action is desirable or required, inasmuch as the gels tend to release the acid slowly. However, the gelled nitric acid compositions of this invention have been found to have particular utility as explosives, and as described more fully hereinafter, they are readily formulated to meet the specific requirements of such use.

As can readily be seen from Example 97, the gelled nitric acid systems are markedly superior to any of the thickened nitric acids proposed in the prior art, for example, compositions thickened by polymethyl methacrylates of molecular weights within the range of 50,000–500,000, or copolymers of methylvinylether and maleic anhydride (e.g., mol wt.$\approx 1.25\times 10^6$). The compositions of this invention are characterized by viscosities within the range of about from 100,000 to over 20 million cps., preferably 200,000 to 5 million cps., values about 10,000 times greater than those compositions based on the thickened nitric acid heretofore known. In addition to improvement in consistency and solids dispersion as compared with the prior art, it should be noted the compositions of this invention can be formulated more rapidly than prior art thickened compositions since, as shown by Example 97, they do not require long dissolution times and, in general, particularly with the preferred compositions, attain substantially full viscosity in a manner of seconds or minutes. That the monomers used in this invention even polymerize in the highly acidic (pH<1) nitric acid environment is, per se, quite unexpected. Inherent safety, though, e.g., freedom from spilling, splashing and leaking together with reduced fuming, is another distinguishing characteristic of the products of this invention.

Several of the gelled nitric acid compositions described above are inherently satisfactory as detonating explosives with further additives, i.e., they can be detonated with moderate-strength primers in diameters of 6 inches or less under moderate conditions of confinement, such as provided by a borehole or a container of moderate wall thickness. However, preferably for explosive applications, the compositions of this invention also contain one or more fuels and/or non-explosive sensitizers which are compatible with (stable in) the nitric acid of the strength used in preparing the gels. Examples of non-explosive fuels are the mono- and dinitro aromatic hydrocarbons, such as nitrobenzene, o-mononitrotoluene and dinitrotoluene; liquid and solid hydrocarbons and hydrocarbon fractions, particularly refined petroleum and mineral oils and the aromatic hydrocarbons, such as benzene, toluene, and the xylenes; carbohydrates, including various cellulose and starch products, e.g., cornstarch, potato starch, wood and paper pulps and sugar; siliceous fuels, including silicon itself and mixtures and alloys of silicon with heavy metals, e.g., ferrosilicon; and sulfur. Light metal fuels such as aluminum also are potentially useful in some of the gelled compositions, provided that they are, or can be made, sufficiently resistant to attack by the nitric acid. The gel copolymer per se acts as a fuel and except as otherwise indicated is included in calculating the amount of non-explosive fuel and oxygen balance. Ordinarily, the gels for use as explosive compositions will be formulated to have an oxygen balance of about from −25 to +10%. Surfactants can be employed to insure complete dispersion of some fuels, e.g., the petroleum and mineral oils, in the explosive composition.

In addition to the non-explosive fuels and/or sensitizers named above the explosive compositions of this invention can, if desired, contain an additive of the art-recognized self-explosive type, provided that such additive is stable in the strengths of nitric acid used in preparing the gels. TNT, for examples, exhibits a high degree of stability in all strengths of aqueous nitric acid and hence is a particularly useful additive of the "self-explosive" type. Examples of other "self-explosive" components which can be used in the gelled nitric acid based compositions of this invention are RDX, nitrocellulose, smokeless power, and other organic nitramines, nitrates and nitrocompounds. For reasons of economy and compatibility, TNT is preferred for use in the compositions of this invention. The TNT or its mixtures (e.g., with ammonium or sodium nitrate) can be introduced into the compositions in the form of crystals, grains, pellets, flakes, or other particulate form which allows ready dispersion thereof. In general, up to 85%, and preferably up to 40%, by weight of self-explosive additive based on weight of the composition is used.

In further addition to the fuels and/or sensitizers discussed above, the explosive compositions of this invention can contain up to about 85%, and preferably 5 to 50%, based on the total weight of composition, of an inorganic oxidizing salt, particularly an inorganic nitrate salt such as ammonium or sodium nitrate. The presence of such salt assists in the in situ polymerization of some of the nitric acid compositions, particularly of compositions based on

nitric acid of greater than about 80% strength and, also, contributes to the explosive energy of the formulation. At least part of the salt, when used, will be dissolved in the system; however, some of the salt can be undissolved providing that it is uniformly distributed throughout the gelled nitric acid matrix.

Stable, gelled nitric acid compositions found especially economical and efficient as detonating explosives comprise a uniform blend of:

(a) About from 25 to 95% by weight of aqueous nitric acid having a strength of from about 40 to 99%, and preferably 60 to 97%;

(b) About from 5 to 30% of a non-explosive fuel, preferably selected from siliceous fuels, light metals, liquid and solid hydrocarbons, carbohydrates, sulfur, mono- and dinitro aromatic hydrocarbons, and mixtures of such fuels and/or sensitizers;

(c) 0 to about 40% of a self-explosive sensitizer, particularly TNT;

(d) 0 to about 50% of an inorganic oxidizing salt, typically, an inorganic nitrate; and

(e) An in situ copolymerization product of

(1) About from 1 to 20% and preferably 2 to 10%, based on the weight of aqueous nitric acid, of at least one monoethylenically unsaturated monomer, as defined above, which preferably is acrylamide, acrylonitrile, methacrylonitrile, acrylic acid, methacrylic acid, methyl acrylate, methacrylamide or a mixture of two or more of these monoethylenically unsaturated monomers of this group, and

(2) About from 1 to 20% and preferably 2 to 15% by weight based on component (1) of a polyethylenically unsaturated monomer, which preferably is N,N'-methylenebisacrylamide, N,N' - hexamethylenebisacrylamide, N,N'-decamethylenebisacrylamide, N,N',N''-triacrylhexahydro-s-triazine, trimethylolpropane trimethacrylate, or ethylene glycol dimethacrylate.

In addition to the aforementioned oxygen balance of −25 to +10%, optimum explosive properties also have been found to be achieved when these gels contain a maximum of about 40% by weight of water, on a total composition basis.

In general, the gelled nitric acid-based blasting compositions of this invention are prepared by blending of the ingredients, e.g., in a rotary type mixer such as a "Lightnin" AG–100 mixer, keeping in mind the same general considerations for the control of the process as were discussed above. As mentioned, it is generally preferred to sparge the nitric acid with an inert gas such as nitrogen or carbon dioxide, e.g., for about 15 minutes, before it is incorporated with other components of the composition and to maintain the components while being blended under an inert atmosphere until polymerization is complete. Particularly when making large volume mixes, e.g., greater than about 25 to 50 lbs., it is desirable to provide a means to remove heat of polymerization or other secondary effects. In practice, sufficient cooling is usually provided by placing the vessel in which the components are being blended or mixed in a bath of cooling water, typically at about 15 to 20° C., the volume of water surrounding the vessel being approximately at least twice the volume of the composition to be prepared in the vessel. Alternatively, cooling can be provided by pumping coolant around the vessel. Usually, the sparged nitric acid is introduced into the cooled mixing vessel first and the other ingredients added individually thereto while the contents of the vessel are being agitated. Polymerization promoters, including reductants such as hydrazine, hydroxylamine, or carbohydrazide, are usually the last ingredients added. Agitation is usually continued until after the composition is gelled, particularly when the added fuels or sensitizers are solids such as for example, ferrosilicon, sulfur, aluminum, silicon, or starch, which must be distributed uniformly throughout the gel matrix. Where fuels or other additives of marginal stability or additives which inhibit polymerization are to be incorporated in the compositions, all ingredients except such additives can be mixed and gelled as previously described, then such additives blended with the finished gel.

As indicated above, for explosive applications preferred ranges of nitric acid strength are from about 60% (corresponding to a maximum water content of about 40%) to 97%. In general, the unit or bulk strength of an explosive composition based on gelled nitric acid increases with increasing strength of the nitric acid gelled. Accordingly gels of nitric acid of 85% strength or higher are usually employed where high bulk strength is a requisite, e.g., in the bottom of a borehole. The bulk or unit strength of an explosive composition, its relative ease of initiation, and its minimum critical diameter can also be regulated to a large degree by the type and quantity of fuel and/or sensitizer employed. In general, a solid fuel such as ferrosilicon, sulfur or siliceous fuels is used to increase the bulk strength of a composition. Organic nitro compounds, typically mononitrotoluene, or dinitrotoluene or, in particular a self-explosive composition, especially TNT, are incorporated to provide compositions which are easily initiated, e.g., by a relatively small primer or by a blasting cap, in some cases, in small diameters. In many cases, a combination of fuels will be employed within the range of proportions indicated to give a composition having the desired physical and explosive properties.

Preferred gelling systems for explosive compositions comprise as the monoethylenically unsaturated monomer acrylonitrile or acrylamide, either used alone or in admixture with acrylic or methacrylic acid. The polyethylenically unsaturated monomer preferred is N,N'-methylenebisacrylamide, N,N'-hexamethylenebisacrylamide, N,N'-decamethylenebisacrylamide, trimethylolpropane trimethacrylate, or ethylene glycol dimethacrylate. In addition to being readily available at reasonable cost, these compositions are particularly effective in providing firm cohesive gels having viscosities within the desired range of 100,000 to 5 million cps., high surface tension as evidenced by lack of stickiness or tackiness, ready workability, flexibility, water resistance, and other desirable physical characteristics in the as-made state. Further, blasting agents including these preferred gelling systems retain their initial physical and explosive properties during storage after production. The preferred gelling systems also allow relatively wide latitude in the consistency of the explosive product made, to fit the needs of a particular type of blasting.

The compositions of this invention can be packaged in containers compatible with the gelled nitric acid, e.g., of polyethylene, polypropylene, or aluminum, and stored until time of use without deterioration, "gassing" or separation of components. Sometimes, at the time of use the explosive compositions are stripped from their containers and loaded directly into the borehole. Such a "shucking" operation is possible with the non-tacky flexible gels of this invention. Even when freed from the container these compositions retain a high degree of resistance to disintegration and leaching by water which may be present in the borehole or which may enter the borehole after the compositions are loaded. Alternatively, the compositions can be prepared at the site of use and pumped or dumped directly into the borehole, which can be lined with a material such as polyethylene, which is both water-impervious and compatible with the gelled nitric acid. When such is the case, it is usually desirable that all components of the composition be liquid for ease of mixing and pumping the composition. Usually, the compositions to be pumped will be less viscous than those to be shucked from their containers and accordingly will comprise somewhat less of the copolymer.

The explosive initiation system used with the gelled nitric acid-based explosive compositions of this invention naturally will be one which is compatible with nitric

acid. To this end, the detonators, i.e., blasting caps, or boosters used in the assembly (explosive train), will preferably have shells of a metal such as aluminum or stainless steel or of, or coated by, a plastic such as polyethylene, polytetrafluoroethylene, polyoxymethylene, or polypropylene. Detonating fuse or electric lead wires extending to the cap and exposed to the gelled nitric acid compositions will usually be provided with a protective coating such as polyethylene, polytetrafluoroethylene, polyoxymethylene ("Delrin"), or polypropylene, which is resistant to attack by nitric acid. The primer charge used with the charge can be a pressed pellet, e.g., of TNT or RDX, or a gelled nitric acid based explosive composition made suitably sensitive to actuation, e.g., by "Primacord," by the incorporation of such ingredients as grained TNT or by the use of acid of higher strength. Such primer charges of gelled nitric acid compositions typically will be in a cartridge of a high-strength plastic such as polyethylene or polypropylene, which is also compatible with nitric acid.

In the following examples which illustrate this invention, parts, percentages and ratios are by weight unless otherwise indicated. In the following examples, the terms noted below mean the following:

Firm—Viscosity of about from 1 million to 3 million centipoise (cps.) measured with a TE spindle at 1.0 r.p.m. on a Brookfield Synchro-lectric Viscometer, Model RVT, with helipath attachment.

Medium firm—Viscosity of about from 400,000 to 1 million cps. using the same conditions of measurement on the Viscometer.

Very firm—Viscosity of about from 3 million to 10 million cps. as measured with TF[1] spindle at 0.5 r.p.m.[1] on the Brookfield Synchro-lectric Viscometer.

"Cheese-like gels"—Viscosity of about from 10 million to 20 million cps. with some conditions of measurement as for "very firm" gels.

"Weak gels"—Viscosities generally less than about 400,000 cps. generally 200,000 to 400,000 cps.

Examples 1 to 76 below illustrate compositions of this invention containing various strengths of nitric acid, salt-containing and salt-free systems, use of various mono- and polyunsaturated components and several promoter systems.

Examples 1 to 76

Gelled aqueous nitric acid compositions of this invention are prepared from the materials noted in Table I. First the nitric acid is sparged with nitrogen to remove nitrogen oxides and oxygen. The mono- and polyunsaturated monomer, together with salt, where noted, are then dissolved in the aqueous nitric acid. Next, the promoter system indicated is added and mixing continued at a temperature of about 20 to 30° C., except where otherwise indicated, e.g., for low monomer concentrations such as in Examples 61–63, mixing is continued at temperatures of about 15° C., until polymerization is substantially complete. In the case of compositions containing dissolved salts and those of nitric acid of greater than 80% strength, the reaction temperature is held within about from 15 to 20° C. In the promoter systems $(S_2O_8)^{-2}$ is added as ammonium persulfate, Cu^{+2} as copper (II) sulfate pentahydrate, hydrazine as hydrazine monohydrate (0.5 molar concentration) and Ag^{+} as silver nitrate. All polymerizations are carried out under a nitrogen blanket. Gelation time refers to the interval between the addition of the last component of the promoter system to the nitric acid and the first appearance of gelled copolymerizaion product in the reaction mass. Except where otherwise noted, none of the gel products shows visible indication of deterioration at ambient temperatures (ca. 20–25° C.) over times of 1 to 7 days, the maximum periods of observation.

[1] Change in spindle and r.p.m. necessary to obtain accurate readings.

TABLE I

Example Number	Aq. HNO_3 Strength, Percent	Copolymers: (a) Monounsatd. Monomer Mat'l, Percent of HNO_3	Copolymers: (b) Polyunsatd. Monomer Mat'l, Percent of (a)	Salt Mat'l, Percent of Aq. HNO_3	Promoter: $S_2O_8^{-2}$, Percent Total Monomer	Promoter: Auxiliary Promoter Mat'l, Ratio of Mat'l/$S_2O_8^{-2}$	Gel Product Description
1	70	ACRN,[1] 5.0	MBAA,[2] 16.6		3.6	N_2H_4, 0.1; Cu^{+2}, 0.05	Firm gel formed in 11 min.
2	70	ACRN, 3.3	MBAA, 25.0		5.0	N_2H_4, 0.1; Cu^{+2}, 0.05	Medium gel formed in 10 min.
3	70	ACRN, 6.6	MBAA, 12.5		1.7	N_2H_4, 0.2; Cu^{+2}, 0.15	Soft gel formed in 18 min.
4	70	ACRN, 6.6	MBAA, 12.5		2.8	N_2H_4, 0.40; Cu^{+2}, 0.05	Very firm gel formed in 7 min.
5	45	ACRN, 6.6	MBAA, 9.0		2.3	N_2H_4, 0.10; Cu^{+2}, 0.05	Firm, but spongy gel containing precipitated solids formed in 10 min.
6	70	ACRN, 4.8	MBAA, 8.3	NH_4NO_3, 20	2.0	N_2H_4, 0.10; Cu^{+2}, 0.15	Firm gel in 13 min.
7	70	ACRN, 4.8	MBAA, 12.5	KNO_3, 8	4.0	N_2H_4, 0.10; Cu^{+2}, 0.05	Firm gel in 9 min.
8	70	ACRN, 10.0	MBAA, 9.0		0.8	Ag^{+1}, 3.00	Firm gel in 3 hrs.
9	75	AA,[3] 5.6	MBAA, 10.7	NH_4NO_3, 2	1.5	N_2H_4, 0.70; Cu^{+2}, 0.10	Firm gel in 2 min.
10	78	AA, 5.6	MBAA, 10.7	KNO_3, 10	1.5	N_2H_4, 0.07; Cu^{+2}, 0.10	Firm gel in 1 min.
11	82.5	AA, 5.6	MBAA, 10.7	KOAc, 10	5.0	N_2H_4, 0.02; Cu^{+2}, 0.03	Do.
12	82.5	AA, 5.6	MBAA, 10.7	NH_4NO_3, 10	5.0	N_2H_4, 0.02; Cu^{+2}, 0.03	Firm gel in 2 min.
13	86	AA, 10.0	MBAA, 10.0	NH_4NO_3, 10	4.0	N_2H_4, 0.02; Cu^{+2}, 0.03	Firm gel in 20 sec.
14	97	AA, 6.2	MBAA, 10.0	NH_4NO_3, 60	6.8	Cu^{+2}, 0.02	Firm gel in 23 min.
15	97	AA, 10.0	MBAA, 10.0	NH_4OAc, 48[4]	4.0	Cu^{+2}, 0.02	Very firm gel in 10 min.
16	97	AA, 10.0	MBAA, 10.0	KH_2PO_4, 40	4.5	Cu^{+2}, 0.02	Medium firm gel in 40 min.
17	97	AA, 10.0	MBAA, 10.0	$(NH_4)_2SO_4$, 44[4]	4.5	Cu^{+2}, 0.02	Very firm gel in 28 min.
18	86	AA, 6.0	MBAA, 10.0	K_2SO_4, 20	6.0	N_2H_4, 0.02; Cu^{+2}, 0.10	Firm gel in 6 min.
19	90	AA, 10.0	MBAA, 10.0	NH_4NO_3, 20	3.6	N_2H_4, 0.02; Cu^{+2}, 0.10	Firm gel in 5 sec.
20	70	AA, 5.0	MBAA, 4.0		1.6	Ag^{+1}, 1.8	Firm gel in 5 min.
21	70	AA, 6.0	MBAA, 7.0		2.6	H_2O_2, 8.0	Weak gel in 30 min; firm gel in 45 min.
22	70	ACRN, 1.7	MBAA, 11.0		5.0	N_2H_4, 0.12; Cu^{+2}, 0.05	Resilient medium firm gel in 12 min.
23	70	ACRN, 3.3; AA, 1.0	MBAA, 10		4.0	N_2H_4, 0.10; Cu^{+2}, 0.05	Medium firm gel in 12 min.

TABLE I—Continued

Example Number	Aq. HNO_3 Strength, Percent	Copolymers: (a) Monounsatd. Monomer Mat'l, Percent of HNO_3	Copolymers: (b) Polyunsatd. Monomer Mat'l, Percent of (a)	Salt Mat'l, Percent of Aq. HNO_3	Promoter: $S_2O_8^{-2}$, Percent Total Monomer	Promoter: Auxiliary Promoter Mat'l, Ratio of Mat'l/$S_2O_8^{-2}$	Gel Product Description
24	60	ACRN, 3.2; AA, 1.0	MBAA, 9.5		2.0	N_2H_4, 0.30; Cu^{+2}, 0.12	Resilient, firm gel in 27 min.
25	29	ACRN, 3.2; AA, 1.0	MBAA, 9.5		2.0	N_2H_4, 0.30; Cu^{+2}, 0.12	Very weak gel after 24 hrs.
26	70	ACRN, 3.2; AA, 1.0	MBAA, 9.5	NH_4NO_3, 2	3.0	N_2H_4, 0.20; Cu^{+2}, 0.08	Medium firm gel in 12 min. Not stable over 1 day.
27	70	ACRN, 3.2; AA, 1.0	MBAA, 9.5	NH_4NO_3, 29	3.0	N_2H_4, 0.20; Cu^{+2}, 0.08	Firm gel in 20 min.
28	70	ACRN, 3.2; AA, 1.0	MBAA, 9.5	NH_4NO_3, 62	3.0	N_2H_4, 0.20; Cu^{+2}, 0.08	Medium firm gel in 32 min.
29	70	ACRN, 1.6; ACRA,[5] 4.0	MBAA, 10.7		2.0	N_2H_4, 0.12; Cu^{+2}, 0.05	Firm gel in 4 min.
30	31	ACRN, 3.2; ACRA, 1.2	MBAA, 9.0		1.3	N_2H_4, 0.25; Cu^{+2}, 0.15	Medium firm gel of low strength in 3 hrs.
31	73	ACRN, 4.0; ACRA, 1.2	MBAA, 11.5	NH_4NO_3, 20	2.7	N_2H_4, 0.10; Cu^{+2}, 0.60	Firm gel in 6 min.
32	70	ACRA, 3.2; AA, 4.0	MBAA, 5.5		1.7	N_2H_4, 0.20; Cu^{+2}, 0.30	Firm gel in 1 min.
33	70	MACRA,[6] 3.2; AA, 3.2	MBAA, 6.3		1.9	N_2H_4, 0.20; Cu^{+2}, 0.30	Do.
34	70	ACRA, 4.0; MeACRA,[7] 4.0	MBAA, 10.0		1.5	N_2H_4, 0.30; Cu^{+2}, 0.05	Firm gel in ½ min.
35	82.5	ACRA, 6.0; MeACRA, 6.0	MBAA, 13.3		3.5	N_2H_4, 0.05; Cu^{+2}, 0.02	Firm gel in 15 min.
36	82.5	ACRA, 6.0; AA, 6.0	MBAA, 13.3		3.5	N_2H_4, 0.15; Cu^{+2}, 0.02	Firm gel formed essentially instantaneously.
37	70	ACRN, 3.3; MACRA, 1.2	MBAA, 9.0	NH_4NO_3, 12.5	1.3	N_2H_4, 0.25; Cu^{+2}, 0.15	Medium firm gel in 34 min.
38	70	ACRN, 3.3; ACRA, 1.2	MBAA, 9.0	NH_4NO_3, 12.5	1.3	N_2H_4, 0.25; Cu^{+2}, 0.15	Firm gel in 10–15 min.
39	70	ACRN, 3.3; MeACRA, 2.0	MBAA, 7.7	NH_4NO_3, 12.5	1.0	N_2H_4, 0.25; Cu^{+2}, 0.15	Firm gel in 14 min.
40	82.5	ACRA, 4.0; MeACRA, 4.0	MBAA, 10.0	NH_4NO_3, 8	5.0	N_2H_4, 0.10; Cu^{+2}, 0.02	Firm gel in 0.5 min.
41	97	ACRA, 6.0; MeACRA, 6.0	MBAA, 13.3	NH_4NO_3, 16	3.5	N_2H_4, 0.10; Cu^{+2}, 0.02	Medium firm gel in 20 min.
42	70	ACRA, 4.2; AA, 1.7	MBAA, 7.0		10.6	Ag^{+1}, 0.4	Firm gel in 4 min.
43	70	MeACRA, 4.2; AA, 1.7	MBAA, 7.0		10.6	Ag^{+1}, 0.4	Firm gel in 5.5 min.
44	70	AA, 3.1	TAHT,[8] 10.0		2.0	N_2H_4, 0.10; Cu^{+2}, 0.15	Firm gel in 4 min.
45	65	ACRN, 4.6; ACRA, 1.4	TAHT, 9.3		1.0	N_2H_4, 0.20; Cu^{+2}, 0.15	Medium firm gel in 50 min.
46	70	ACRN, 6.6	TMDM,[9] 12.2		1.0	N^2H_4, 0.20; Cu^{+2}, 0.15	Weak, flowing gel in 23 min.
47	70	AA, 4.1	TMDM, 10.0		0.8	N_2H_4, 0.20; Cu^{+2}, 0.30	Medium firm gel in 3 min.
48	70	AA, 4.1	TMPTM,[10] 10.0		0.8	N_2H_4, 0.20; Cu^{+2}, 0.30	Medium firm gel in ca. 6 min.
49	86	AA, 8.0	TAHT, 10.0	NH_4NO_3, 14	3.6	N_2H_4, 0.02; Cu^{+2}, 0.03	Firm gel in 20 sec.
50	97	AA, 10.4	TAHT, 10.0	NH_4NO_3, 40	4.0	Cu^{+2}, 0.02	Firm gel in 6 min.
51	70	ACRN, 4.8; ACRA, 1.7	TAHT, 9.3	NH_4NO_3, 12.5	1.0	N_2H_4, 0.20; Cu^{+2}, 0.15	Firm gel in 35 min.
52	70	AA, 6.0	TMDM, 7.0		1.6	Ag^{+1}, 3.75	Firm gel in 8 min.
53	70	AA, 6.0	TMPTM, 7.0		1.6	Ag^{+1}, 3.75	Firm gel in 5 min.
54	70	AA, 6.0	EGDM,[11] 7.0		1.6	Ag^{+1}, 3.75	Firm gel in 4¾ min.
55	70	AA, 5.8	MBAA, 7.1		1.0	$(NH_2OH)_2$—H_2SO_4, 0.50; Cu^{+2}, 0.15	Firm gel in 18 min.
56	70	AA, 5.8	MBAA, 7.0		2.5	$CO(NHNH_2)_2$, 0.50; Cu^{+2}, 0.15	Firm gel in 40 min.
57	70	AA, 5.0	MBAA, 4.0		1.6	Co^{+2}, 1.00	Weak gel in 2½ hr.
58	80	AA, 4.0	MBAA, 10.0		9.0	N_2H_4, 0.02; Cu^{+2}, 0.1	Firm gel in 42 sec.
59	90	AA, 16.0	MBAA, 15.0		2.2	N_2H_4, 0.02; Cu^{+2}, 0.1	Weak gel in 20 min; firm gel in 30 min.
60	78	ACRN, 4.0	MBAA, 11.5	NH_4NO_3, 4.0	2.7	N_2H_4, 0.10; Cu^{+2}, 0.60	Firm gel in 6 min.
61[12]	70	AA, 2	MBAA, 10.0		5.3	N_2H_4, 0.04; Cu^{+2}, 0.09	Firm gel in 5 min.
62[12]	70	AA, 1.5	MBAA, 10.0		14.3	N_2H_4, 0.04; Cu^{+2}, 0.05	Firm gel in 4½ min.
63[12]	30	AA, 1.25	MBAA, 30.0		28.0	N_2H_4, 0.03; Cu^{+2}, 0.03	Weak gel in 3 hrs.
64[12]	70	4-vinylpyridine, 8	MBAA, 10		7	N_2H_4, 0.04; Cu^{+2}, 0.03	Firm gel in 2.5 hrs.
65[12]	70	4-vinylpyridine, 8	Divinylbenzene, 10		7	N_2H_4, 0.04; Cu^{+2}, 0.03	Weak gel in 18 hrs.
66[12]	70	2-methyl-5-vinylpyridine, 8	MBAA, 10		7	N_2H_4, 0.04; Cu^{+2}, 0.03	Firm gel in 1 hr.
67[12]	70	Acrylamide, 4	Allylacrylate, 20		3	N_2H_4, 0.04; Cu^{+2}, 0.08	Firm, crumbly gel in 20 min.
68[12]	70	do	N-allylmethacrylamide, 20		3	N_2H_4, 0.04; Cu^{+2}, 0.08	Firm gel in 1 hr.
69[12]	70	do	Diallylether, 20		6	N_2H_4, 0.04; Cu^{+2}, 0.04	Firm gel in 30 min.
70[12]	70	do	Diallyladipate, 27.5		5	N_2H_4, 0.04; Cu^{+2}, 0.04	Firm gel in 8 min.
71[12]	70	do	Diallyl maleate, 20		6	N_2H_4, 0.04; Cu^{+2}, 0.04	Very firm gel in 4 min.
72[12]	70	do	Diallyl ether of pentaerythritol, 27.5		5	N_2H_4, 0.04; Cu^{+2}, 0.04	Firm gel in 20 min.
73[12]	70	do	Diallylamine, 27.5	NH_4NO_3, 13	5	N_2H_4, 0.04; Cu^{+2}, 0.04	Medinm firm gel in 35 min.
74[12]	70	do	N,N′-diallyladipamide, 20		6	N_2H_4, 0.04; Cu^{+2}, 0.04	Firm gel in 15 min.
75[12]	70	do	N-allylacrylamide, 20		6	N_2H_4, 0.04; Cu^{+2}, 0.04	Firm gel in 37 min.
76[12]	70	do	Vinyl methacrylate, 20		6	N_2H_4, 0.04; Cu^{+2}, 0.04	Medium firm gel in 2 hrs., 20 min.

[1] ACRN—acrylonitrile.
[2] MBAA—N,N′-methylenebisacrylamide.
[3] AA—acrylamide.
[4] Not completely dissolved in HNO_3.
[5] ACRA—acrylic acid.
[6] MACRA—methacrylic acid.
[7] MeACRA—methyl acrylate.
[8] TAHT—N,N′,N″-triacrylylhexahydro-s-triazine.
[9] TMDM—tetramethylene glycol dimethacrylate.
[10] TMPTM—trimethylolpropanetrimethacrylate.
[11] EGDM—ethylene glycol dimethacrylate.
[12] Reaction mixture maintained at about 15° C. during mixing of ingredients and polymerization.

Similar results are obtained when the compositions are gelled by the in situ polymerization in nitric acid of sodium, potassium and ammonium acrylates, cyclohexyl methacrylate, α-cyanoethyl acrylonitrile, or 2-hydroxy ethylacrylate, each with N,N'-methylenebisacrylamide in the general amounts and by the procedure shown above. In a like manner, similar results are also obtained when the promoter for the in-situ polymerization comprises perborate and pervanadate ions.

Examples 77–86

Gelled nitric acid compositions are prepared by the method described above for Examples 1–76, each composition being gelled to a weak gel by the in situ polymerization in 70% nitric acid, of acrylamide with the cross-linking monomer indicated in Table II, using a promoter system comprising $[S_2O_8]^{-2}$, hydrazine, and Cu^{+2}. Samples of the gels formed are stored at room temperature (nominally 25° C.) and at 45° C. For accelerated test purposes gels are deliberately formed using low concentrations of monomer so that the decomposition characteristics of the gel can be determined more rapidly. The characteristics of each gel after storage are summarized in Table II. Although the gels decompose in time, as formed they are useful for the purposes described hereinbefore. As seen from the attached table, gel life is markedly prolonged when bisacrylamides having a long alkylidene chain, preferably of 6 to 10 carbons, between the functional groups is used. Gel life can be extended also by using more of the polymerizable monomers, although at equivalent concentrations the aforementioned improvement still pertains.

TABLE II

Example Number	Acrylamide, percent of HNO_3	Polyunsaturated Monomer, percent of Acrylamide	Storage Temperature	Characteristics of Gel After Storage
77	3	Methylenebisacrylamide, 4.6	Room	Liquid in 13 days.
78	2	Methylenebisacrylamide, 7	do	Liquid in 3 days.
79	2	Methylenebisacrylamide, 7	45° C	Liquid in 18 hr.
80	3	Trimethylenebisacrylamide, 5.3	Room	Liquid in 14 days.
81	2	Trimethylenebisacrylamide, 8	do	Weak gel in 3 days.
82	3	Hexamethylenebisacrylamide, 6.6	do	Liquid in 20 days.
83	2	Hexamethylenebisacrylamide, 10	do	Medium firm gel in 3 days.
84	2	Hexamethylenebisacrylamide, 10	45° C	Liquid in 4.5 days.
85	2	Decamethylenebisacrylamide, 12.5	Room	Firm gel in 3 days.
86	3	Decamethylenebisacrylamide, 6	45° C	Liquid in 4 days.

Examples 87–96

Gelled nitric acid compositions are prepared by the method described above for Examples 1–75, each composition being gelled by the in situ polymerization in nitric acid of the strength indicated in Table III of acrylamide (7% based on weight of aq. HNO_3) and MBAA (10% by weight of acrylamide) in the presence of promoter systems as indicated in Table III.

TABLE III

Example	Acid Strength, Percent	Promoter Material, Percent Used	Gel Product Description
87	20	$(NH_4)_2S_2O_8$, 6% of monomers $Fe(NH_4)_2(SO_4)_2.6H_2O$, 10% of $S_2O_8^{-2}$.	Firm gel in 2 sec.
88	40	do	Firm gel formed instantaneously.
89	50	do	Medium firm gel in 11 sec.
90	30	H_2O_2, 2% of monomers $Fe(NH_4)_2(SO_4)_2.6H_2O$, 30% of H_2O_2.	Medium firm gel formed instantaneously.
91	40	α,α'-azobis(α,γ-dimethyl-γ-methoxyvaleronitrile), 3% of monomers.	Firm gel in 3.5 min.
92	40	Peracetic acid, 1.2% of monomers $Fe(NH_4)_2(SO_4)_2.6H_2O$, 50% of peracetic acid.	Weak gel in 8 min.
93	40	tert-Butylhydrogen peroxide, 3% of monomers $Fe(NH_4)_2(SO_4)_2.6H_2O$, 20% of peroxide.	Firm gel essentially instantaneously.
94	50	Cobaltic sulfate (hydrous) 5–10% of monomers (Co^{+3}, 0.8–1.6% of monomers).	Firm gel in 15 min.
95	70	Cobaltic sulfate (hydrous) 2.5–5% of monomers (Co^{+3}, 0.4–0.8% of monomers) ($N_2H_4.H_2O$, 4% of cobaltic sulfate) (N_2H_4/Co^{+3}, .005–.01).	Firm gel in 1 min.
96	70	Cobaltic sulfate (hydrous) 6.2% of monomers Co^{+3}, 1.5% of monomers $(NH_4)_2S_2O_8$, 70% of cobaltic sulfate.	Firm gel in 80 sec.

The following example compares in situ polymerized compositions of this invention with aqueous nitric acid compositions thickened with prepolymerized vinyl polymers.

Example 97

In 240 parts of nitrogen-sparged 70% nitric acid are dissolved 7.5 parts of acrylamide (3% based on the aqueous nitric acid) and 0.5 part of N,N'-methylenebisacrylamide. Next, promoter consisting of 0.1 part of $(NH_4)_2S_2O_3$. 0.1 part of $CuSO_4 \cdot 5H_2O$ and 0.006 part of $N_2H_4 \cdot H_2O$ are added and mixing and polymerization continued under a nitrogen blanket at about 20 to 25° C. A firm gel is obtained in about 165 sec. After 30 minutes and 24 hours, respectively, the viscosity of the gel is 500,000 cps. and 400,000 cps. as measured on a Brookfield Synchro-lectric Viscometer, Model RVT, with a helipath attachment using a TE spindle at 5.0 r.p.m. (at 1.0 r.p.s. the viscosities are 1,400,000 and 1,100,000 cps., respectively).

As a comparison, attempts are made to prepare three thickened 70% aqueous nitric acid compositions by stirring 250 parts of the aqueous acid with 7.5 parts each of a copolymer of methyl vinyl ether and maleic anhydride, having a molecular weight of about 1,250,000 ("Gantrez" AN 169), a homopolymer of methyl methacrylate having a molecular weight of about 400,000 ("Lucite" ®2008). The methyl vinyl ether-maleic anacrylate having a molecular weight of about 50,000 ("Lucite" 2008®). The methyl vinyl ether-maleic anhydride copolymer dissolved in about 45 minutes to yield a thin syrupy liquid having a viscosity of about 120 cps. measured as described above but using a TA spindle at 5.0 r.p.m. The 400,000 mol. wt. polymethyl methacrylate does not dissolve even after two hours stirring. The 50,000 mol. wt. polymethyl methacrylate dissolved in

about 30 minutes to yield a product with no apparent thickening having a viscosity of less than 100 cps. measured with a TA spindle at 5.0 r.p.m.

The following examples exemplify gelled nitric acid compositions particularly designed for use as explosives.

Examples 98 to 103

Six explosive compositions are prepared by in situ polymerization of the formulation summarized in Table IV, each composition being based on the gelation of 70% strength aqueous HNO_3 by the copolymerization product of acrylamide (AA) and N,N'-methylenebisacrylamide (MBAA) effected in the presence of the redox system introduced in the form of $(NH_4)_2S_2O_8$ and $AgNO_3$. Various fuels and sensitizers as shown in Table IV are incorporated in the formulations. These compositions are prepared by the mixing and polymerization procedures outlined above. The compositions are prepared by first thoroughly dispersing all ingredients except the promoters in the aqueous nitric acid, then adding the promoters ($S_2O_8^{-2}$ and Ag^+) and finally continuing mixing at a temperature of about 20 to 25° C. for about 10 to 20 minutes, during which time the polymerization runs substantially to completion. The nitric acid is sparged with nitrogen to remove dissolved oxygen and nitrogen oxides and the combining of ingredients conducted under a blanket of nitrogen to exclude atmospheric oxygen. A nitrogen blanket is maintained over the mix by bleeding nitrogen into a polyethylene bag inverted over the mix pot, the mixer shaft going through the bag.

The percentages and ratios reported in the tables below are on a weight basis; the parts of each ingredient components are reported on the basis of parts by weight of the total composition. Values for the monoethylenically unsaturated monomer, i.e., acrylamide, are given both in terms of weight of the monomer, in terms of the total weight of composition, and in terms of percent by weight of the monomer based on the aqueous nitric acid in the system. Similarly, values for the polyethylenically unsaturated monomer N,N'-methylenebisacrylamide are expressed both in terms of parts by weight of the total composition and in terms of percent by weight of the polyunsaturated monomer based on the weight of the monoethylenically unsaturated monomer.

The gelled formulations are loaded into 2- and 3-inch diameter by 15-inch long glass containers. The density of each charge and detonation velocities are determined by conventional means. In each case, detonation of the charge is effected by a 100-gram RDX pellet booster which is actuated by a conventional Du Pont E–94 blasting cap. The formulations and results of the tests are summarized in Table IV. All of the formulations are firm or medium firm, non-tacky gels.

TABLE IV

Example	98	99	100	101	102	103
Formulation:						
70% aq. HNO_3	73.2	73.2	59.2	79.0	47.8	72.9
Acrylamide	5.6	5.6	4.5	4.7	4.5	3.9
MBAA	0.4	0.4	0.3	0.3	0.3	0.3
$AgNO_3$	0.4	0.4	0.4	0.4	0.4	0.6
$(NH_4)_2S_2O_8$	0.1	0.1	0.1	0.1	0.1	0.1
26° DNT [1]	20.3	20.3				
Mineral Oil [2]				5.5	6.9	
TNT			24.4	10.0		
NH_4NI_3			11.2		30.0	
$NaNO_3$					10.0	
Starch						22.1
Acrylamide, percent of aq. HNO_3	7.7	7.7	7.9	5.9	9.4	5.3
MBAA, percent of acrylamide	7.1	7.1	6.7	6.4	6.7	7.7
Oxygen Balance, percent	−0.7	−0.7	+2.1	0.0	−2.3	0.0
Velocity, m./sec.	7,050	6,140–6,860	3,680	3,790	4,700	5,640
Diameter, in.	2	2	2	3	3	3
Density	1.3	1.4	1.5	1.3	1.3	1.4

[1] DNT—dinitrotoluene (26° transition point).
[2] "Bayol"-F-oil, commercially available from Esso Refining Co.

Examples 104 and 105

Explosive compositions are prepared and tested as described for Examples 98 to 103; however these compositions are gelled in situ by the copolymerization of acrylonitrile (ACRN) and N,N'-methylenebisacrylamide in the presence of $AgNO_3$ and $(NH_4)_2S_2O_8$. The formulations and their physical and explosive characteristics are summarized in Table V.

TABLE V

Example	104	105
ACRN (acrylonitrile)	9.7	7.0
MBAA [1]	1.1	0.8
70% HNO_3	79.8	76.6
$AgNO_3$	0.3	0.3
$(NH_4)_2S_2O_8$	0.5	0.4
Starch		14.9
Nitrobenzene	8.6	
ACRN, percent of HNO_3	12.2	9.1
MBAA, percent of ACRN	11	11
Velocity (m./sec.)	6,640	3,390
Diameter (in.)	1.8	3
Density (g./cc.)	1.3	1.3
Oxygen Balance, percent	−3.5	−0.2
Physical Appearance	[2]	[3]

[1] N, N'-methylenebisacrylamide.
[2] Cheese like gel.
[3] Firm gel.

Example 106

A firm, gelled explosive composition is prepared having the formulation shown in tabular form below by the general procedure shown in Examples 98 to 103. As can be noted, the monounsaturated monomer of the gelation system is the combination of acrylamide and methyl acrylate and the polyunsaturated monomer is again N,N'-methylenebisacrylamide (MBAA).

TABLE VI

Monounsaturated Monomer	3.9
Methyl acrylate	2.8
Acrylamide	1.1
MBAA	0.3
70% HNO_3	29.0
$AgNO_3$	0.3
$(NH_4)_2S_2O_8$	0.6
Mineral oil ("Bayol" F)	6.0
NH_4NO_3	50.0
$NaNO_3$	10.0
Monounsaturated monomers, percent of HNO_3	13.4
MBAA, percent of monounsaturated monomer	7.7
Velocity (m./sec.)	2670
Oxygen balance, percent	+0.1
Density	1.4

Examples 107 to 109

Gelled explosive compositions are prepared by the general procedure shown in Examples 98 to 103 except that in Example 107 the components are mixed and immediately charged to the borehole before gelation has proceeded to any substantial extent. The in situ copolymerization of acrylamide and N,N'-methylenebisacrylamide is effected in the presence of $(NH_4)_2S_2O_8$, $N_2H_4 \cdot H_2O$, added as a solution of ca. 0.5 molar concentration, and $CuSO_4 \cdot 5H_2O$. Three different types of formulations are prepared:

TABLE VII

Examples	107	108	109
Acrylamide	6.7	5.1	5.6
MBAA	0.3	0.3	0.2
$CuSO_4.5H_2O$	0.2	0.1	0.1
$(NH_4)_2S_2O_8$	0.3	0.2	0.3
68.3% HNO_3	75.8	51.3	77.4
26° dinitrotoluene	16.7	13.0	5.0
Ferrosilicon	------	30.0	------
Mineral oil ("Bayol" 52)	------	------	6.4
Starch	------	------	5.0
$N_2H_4.H_2O$	0.01	0.01	0.03
AA, percent of HNO_3	8.8	9.9	7.2
MBAA, percent of AA	4.5	5.9	3.6
Remarks	(1)	(2)	(3)

[1] Formulation gelled in situ in borehole.
[2] Solids suspended in gel.
[3] Oils suspended in gel.

The formulations are loaded into 2½-inch-diameter holes, 12 feet deep, in a limestone formation. The bottom of the borehole contains a primer unit comprising a plastic shell housing a ½-pound liquid explosive booster composition comprising 28% DNT (26°) and 72% HNO_3 (70% strength) which is actuated by a ½-pound charge of pressed TNT initiated by a No. 6 blasting cap having an aluminum shell. After setting the priming charge unit into the borehole, a 4-mil thick liner of polyethylene is lowered into the borehole to contain the main explosive charge. The handling and loading of each charge of the types is described below.

Example 107—The ungelled mix is poured into the borehole liner and allowed to set to a "loose" gel. When actuated by the primer, the charge detonates completely and effectively.

Example 108—This gelled composition, which contains a high loading of an insensitive solid fuel (ferrosilicon), is hard and "cheese-like." The charge detonates at 5100 m./sec., with noticeably more violence than the first formulation.

Example 109—This gelled composition is completely homogeneous and has handling properties such that a large charge (17.4 pounds) can be loaded into the borehole in a few (3) minutes. The charge detonates completely at about 4980 m./sec.

Examples 110–113

Gelled explosive compositions of the formulations tabulated below are prepared and tested basically as described for Examples 98 to 103, the mixing vessels being submerged in (ice) water at 17–20° C. In these compositions, the gelling system is the copolymerization product of acrylamide and N,N'-methylenebisacrylamide prepared in situ in the presence of a $(NH_4)_2 \cdot S_2O_8$, $N_2H_4 \cdot H_2O$ added as a solution of about 0.5 molar concentration, and $CuSO_4 \cdot 5H_2O$. As can be seen, the water content of the composition varies from about 40%, which usually is the maximum allowable to assure reliable propagation of detonation by the composition in 6-inch diameter, to 1% as represented in the formulation comprising HNO_3 of 97% strength. All compositions set up to form cohesive gels within about 3 to 10 minutes.

TABLE VIII

Example	110	111	112	113
97% HNO_3	56.7	54.8	------	------
67.7% HNO_3	------	------	65.3	63.0
Water [1]	------	------	13.4	16.5
Acrylamide	6.7	6.3	6.2	6.0
MBAA	0.7	0.7	0 2	0.2
$CuSO_4.5H_2O$	0.03	0.03	0.2	0.2
$(NH_4)_2S_2O_8$	1.0	1.0	0.4	0.4
$N_2H_4.H_2O$	------	------	0.03	0.03
Oil	8.0	6.6	------	------
Starch	------	4.6	14.3	13.7
NH_4NO_3	26.9	26.0	------	------
Acid Strength	97	97	56.2	53.7
Total Water in compn	1	1	34.5	36.8
Acrylamide, percent of HNO_3	11.8	11.5	11.0	11.1
MBAA, percent of acrylamide	10.5	11.1	3.2	3.3
Detonation Velocity, m./sec	4,310	4,530	4,880	4,706

[1] In addition to that in aq. HNO_3.

Example 114

A firm, gelled explosive composition of this invention indicated below is prepared by the procedure described for Examples 72 to 77. The composition is maintained at about 24° C. during formulation by immersing the mixing vessel in ice water. After formulation the composition is maintained at about 21° C. The in situ polymerization of the acrylamide and N,N'-methylenebisacrylamide is effected in the presence of $(NH_4)_2S_2O_8$ and $CuSO_4 \cdot 5H_2O$. When actuated in a 6-inch diameter column by a 50 g. RDX pellet, the composition detonates completely with considerable brisance, digging a hole in the earth beneath the charge.

97% HNO_3	50.
Acrylamide	3.
MBAA	0.5
NH_4NO_3	26.05
Sulfur	20.
$(NH_4)_2S_2O_8$	0.4
$CuSO_4 \cdot 5H_2O$	0.05
	100.00

Example 115

A mixture of crude acrylamide sulfate and crude methylenebisacrylamide sulfate is formed in the same reaction mixture as follows. Sulfuric acid (471 parts) is charged to a three-necked flask and water (86.5 parts) added dropwise, the temperature rising to 100° C. during the addition. Copper (0.2 part) is added as polymerization inhibitor. The contents of the flask are cooled to 18° C. and 12.0 parts of a 37% formaldehyde solution (4.4 parts) added. Acrylonitrile then is added dropwise until 246 parts is present. During this addition the temperature of the reaction mixture rises to 45° C. After the addition of acrylonitrile is completed, heat is applied until the temperature of the reaction mixture is 120° C. and maintained at this temperature for 10 minutes.

Eighteen (18) parts of the crude reaction product, which comprises 7.02 parts acrylamide and 0.05 part methylenebisacrylamide, is then used to gel 180 parts of ntirogen sparged 75% nitric acid. The promoter consists of 0.15 part $CuSO_4 \cdot 5H_2O$, 0.40 part $(NH_4)_2S_2O_8$, and 0.016 part of $N_2H_4 \cdot H_2O$ and gelation is effected at 20° C. A firm gel is obtained in 4 minutes.

The crude product is also used to form explosive compositions comprising, by weight,

75% nitric acid	82.2
Cornstarch	2.4
Hydrocarbon distillate ("Deo-Base" Oil)	8.2
Acrylamide	3.0
Methylenebisacrylamide	0.1
H_2SO_4	3.7
$CuSO_4 \cdot 5H_2O$	0.07
$(NH_4)_2S_2O_8$	0.18
$N_2H_4 \cdot H_2O$	0.01

The composition forms a firm gel in 10½ minutes at 20° C. When detonated in 5- and 6-inch-diameter at 32° F., in 5-inch-diameter the detonation velocity is 4620 m./sec. and in 6-inch diameter, 5290 m./sec.

Examples 116 and 117

Explosive compositions of the formulations shown below are prepared by the procedures described for Examples 98 to 103. The formulation of Example 116 is prepared from pure acrylamide; Example 117 is identical to that of Example 116 except that the crude product obtained by hydrolysis of acrylonitrile in the presence of H_2SO_4 at 100° C. is used instead of the pure acrylamide, in amounts equivalent to the acrylamide used in Example 116. The compositions are tested as described above. No appreciable difference in gel time or explosive characteristics is observed in the two formulations.

	115	116
Acrylamide	3.3	
MBAA	0.09	0.09
Crude Hydrolysis Product		[1] 7.8
75% HNO_3	83.2	79.2
Hydrocarbon distillate ("Deo-Base" Oil)	10.7	10.2
Starch	2.5	2.4
$CuSO_4.5H_2O$	0.04	0.1
$(NH_4)_2S_2O_8$	0.20	0.2
85% $N_2H_4.H_2O$	0.01	0.01
Gel Time (min.)	9–11	9–12
Detonation Velocity at 32° F. (m./sec.)	5,770	[2] 5,640–5,900

[1] Equivalent to 3.3% acrylamide.
[2] From 5 tests.

I claim:

1. A process for making gelled nitric acid which comprises copolymerizing, in aqueous nitric acid of about from 5 to 99% strength, a mixture of mono- and polyethylenically unsaturated monomers, soluble and stable in the system, said mixture comprising:

(a) about from 1 to 20% by weight, based on the aqueous nitric acid, of monomer selected from at least one of the group consisting of (1) monomers having the formula:

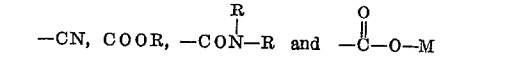


and (2) monovinyl pyridines

and

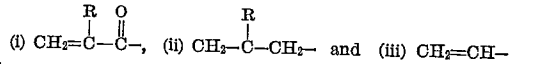
(b) about from 1 to 30% by weight, based on (a), of monomer polymerizable therewith having at least two terminal unsaturated methylene groups,

wherein X is selected from the group consisting of



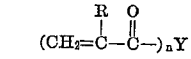
M is alkali or alkaline-earth metal or an ammonium group: and the R's are independently selected from the group consisting of hydrogen, lower alkyl, cycloalkyl, hydroxyalkyl, and cyanoalkyl of 1 to 8 carbons.

2. A process of claim **1** wherein (b) is at least one of the group consisting of (1) polyethylically unsaturated monomers of the formula $[A]_nY$ and (2) divinyl benzenes, wherein the A's are independently selected from the group consisting of



at least one A being (i) or (ii); *n* is 2 to 5 inclusive; and Y is a bridging radical to which a plurality of said unsaturated moieties in (b) are bonded by oxygen or nitrogen in Y; provided that when (b) consists essentially of (b) (2), the monofunctional monomer (a) consists essentially of (a)(2).

3. A process of claim **2** wherein the monofunctional monomer component of (a) is selected from (a)(1) and polyfunctional monomer component (b) is selected from monomers of the formula



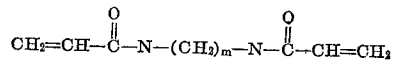
4. A process of claim **3** wherein said nitric acid is of least 30% strength.

5. A process of claim **4** wherein the polymerization mixture additionally contains up to about 60% by weight, based on the aqueous nitric acid, of salt having a first ionization constant in water of at least 10^{-6}.

6. A process of claim **4** wherein the R's bonded to the α-carbon in the unsaturated moieties in the said monomers (a) and (b) are selected from the group consisting of hydrogen and methyl.

7. A process of claim **6** wherein said monomer component (a) is a mixture of acrylonitrile and acrylic acid.

8. A process of claim **6** wherein (a) is acrylamide and (b) is



wherein *m* is 1 to 12, inclusive.

9. A process of claim **6** wherein the polymerization mixture contains a redox promoter couple.

10. A process of claim **9** wherein said promoter comprises persulfate.

11. A process of claim **10** wherein the polymerization mixture additionally contains at least one of the group consisting of hydrazine, hydroxylamine and carbohydrazide as auxiliary promoter.

12. A process of claim **10** wherein said polymerization mixture additionally contains group 1(B) metal ions.

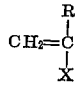
13. A process of claim **4** for making water-bearing explosives which comprises adding to the reaction mixture prior to said in situ polymerization about from 5 to 30%, based on the total weight of the composition, of non-explosive fuel, including monomer components (a) and (b).

14. A process of claim **13** wherein said polymerization is promoted with persulfate.

15. A process of claim **14** wherein said polymerization is additionally promoted with at least one of the group consisting of hydrazine, Cu^{+2} and Ag^{+1}.

16. Stable gelled nitric acid comprising a mixture of about 5 to 99% strength aqueous nitric acid and in situ-polymerized copolymer of

(a) about from 1 to 20% by weight based on the aqueous nitric acid of monomer selected from at least one of the group consisting of (1) monomers having the formula:

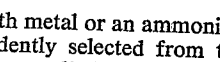


and (2) monovinylpyridines

and

(b) about from 1 to 30% by weight, based on (a), of monomer polymerizable therewith having at least two terminal unsaturated methylene groups,

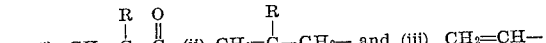
wherein X is selected from the group consisting of



M is alkali or alkaline-earth metal or an ammonium group and the R's are independently selected from the group consisting of hydrogen, lower alkyl, cycloalkyl, hydroxyalkyl and cyanoalkyl of 1 to 8 carbons.

17. A product of claim **16** wherein (b) is at least one of the group consisting of (1) polyethylenically unsaturated monomers of the formula $[A]_nY$ and (2) divinyl ben-

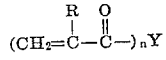
zenes, wherein the A's are independently selected from the group consisting of



(i) $CH_2=\underset{R}{\underset{|}{C}}-\overset{O}{\overset{\|}{C}}$, (ii) $CH_2=\underset{R}{\underset{|}{C}}-CH_2-$ and (iii) $CH_2=CH-$

at least one A being (i) or (ii); n is 2 to 5, inclusive; and Y is a bridging radical to which a plurality of said unsaturated moieties in (b) are bonded by oxygen or nitrogen in Y; provided that when (b) consists essentially of (b)(2), the monofunctional monomer (a) consists essentially of (a)(2).

18. A product of claim **17** wherein the monofunctional component (a) is selected from (a)(1) and the polyfunctional monomer component (b) is selected from monomers of the formula



$$(CH_2=\underset{R}{\underset{|}{C}}-\overset{O}{\overset{\|}{C}}-)_nY$$

19. A gelled nitric acid based composition of claim **18** which comprises up to 85% of TNT and up to 95% of aqueous nitric acid having a strength of about 40 to 99%.

20. A gelled nitric acid-based composition of claim **18**, said composition being an explosive and comprising a uniform blend of:

(a) about from 25 to 95% by weight of aqueous nitric acid having a strength of about from 40 to 99%;

(b) about from 5 to 30% by weight of non-explosive fuel selected from the group consisting of siliceous compounds, light metals, hydrocarbons, sulfur, mono- and dinitro aromatic hydrocarbons, and

(c) in situ copolymerization product of (1) about from 1 to 20% based on the weight of (a) of at least one of the group consisting of acrylamide, methacrylamide, acrylonitrile, methacrylonitrile, acrylic acid, methacrylic acid, methyl acrylate and methyl methacrylate and (2) about from 1 to 20%, based on the weight of (1), of at least one of the group consisting of N,N' - methylenebisacrylamide, N,N' - hexamethylenebisacrylamide, N,N' - decamethylenebisacrylamide, N,N',N'' - triacrylylhexahydro - s - triazine, trimethylol propane trimethacrylate and ethylene glycol dimethacrylate.

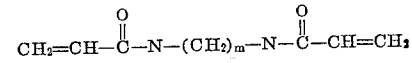
21. An explosive of claim **20** containing up to about 40% by weight of TNT.

22. An explosive of claim **20** containing up to about 50% by weight of inorganic oxidizing salt.

23. An explosive of claim **20** having an oxygen balance of about from −25 to +10.

24. An explosive of claim **20** wherein the in situ polymerization product is a copolymer of acrylonitrile.

25. An explosive of claim **20** wherein said copolymerization product is a copolymer of acrylamide and monomer of the formula



$$CH_2=CH-\overset{O}{\overset{\|}{C}}-N-(CH_2)_m-N-\overset{O}{\overset{\|}{C}}-CH=CH_2$$

wherein m is 1 to 12, inclusive.

26. An explosive of claim **25** wherein m is 6 to 10, inclusive.

27. An explosive of claim **25** wherein said copolymerization product is a copolymer of acrylamide and N,N'-methylenebisacrylamide.

No references cited.

BENJAMIN R. PADGETT, *Primary Examiner.*

UNITED STATES PATENT OFFICE

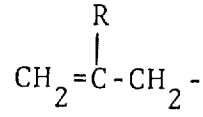
CERTIFICATE OF CORRECTION

Patent No. 3,361,601 January 2, 1968

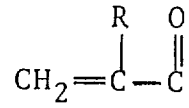
Joseph D. Chrisp

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 25, lines 66 and 67, Formula (ii), should appear as shown below instead of as in the patent:



column 27, lines 17 to 19, Formula (i), should appear as shown below instead of as in the patent:



Signed and sealed this 22nd day of April 1969.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents