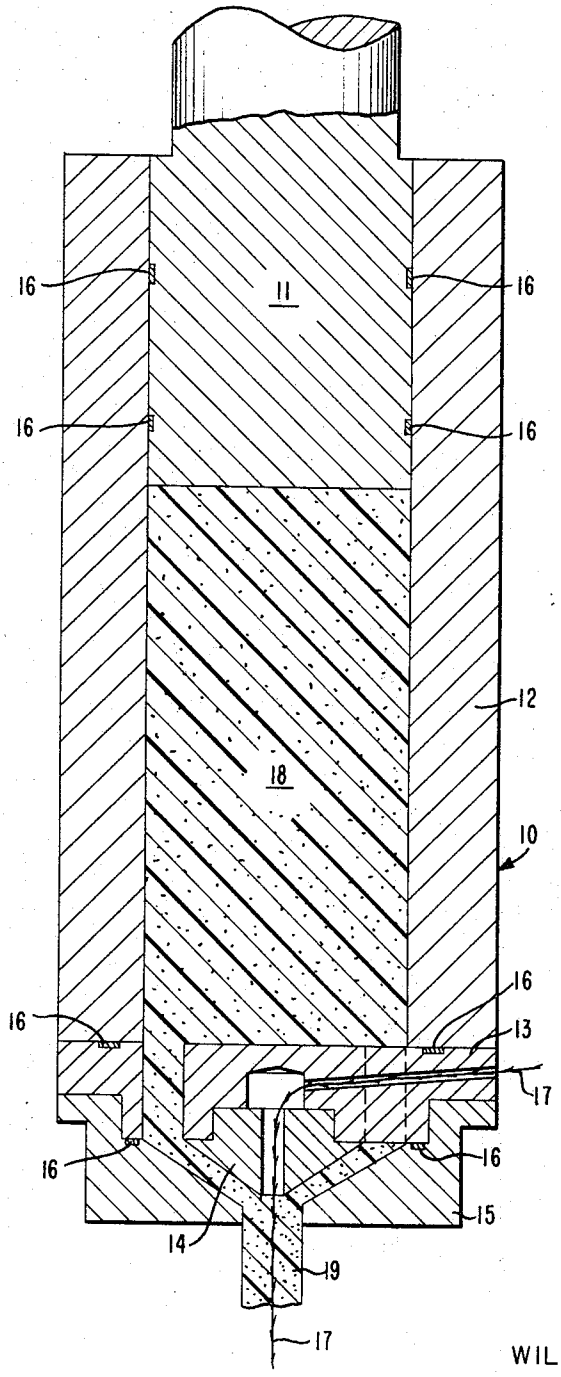
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FLEXIBLE DETONATING COMPOSITIONS CONTAINING HIGH EXPLOSIVES AND POLYMERIC METALLOCARBOXYLATES

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FLEXIBLE DETONATING COMPOSITIONS CONTAINING HIGH EXPLOSIVES AND POLYMERIC METALLOCARBOXYLATES

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This invention relates to novel explosive compositions, to flexible, shaped, detonating articles made from said compositions, and to methods for manufacturing such compositions and articles.

Flexible detonating fuses have been widely employed as priming agents, as conveyors of detonation, generators of shock pressure, and the like, both in commercial and in military applications. Thus, one of the first widely used and practically effective articles of this kind was a detonating fuse known under the name "Cordeau" (U.S. Patent No. 869,219) which consisted of a metal tube, generally of lead or lead alloy, filled with trinitrotoluene. This fuse, however, was relatively low in tensile strength, especially in small diameters; was easily deformed or fractured by mild impacts and by bends because of its low order of resilience, toughness and tensile strength; was relatively heavy per unit of length; was relatively low in initiating power because of the metal sheath surrounding the explosive core; could not be used above about 175° F. because the explosive core melted and became less sensitive; and was expensive to manufacture.

An effective successor to "Cordeau" is a detonating fuse which consists of an explosive core of PETN (pentaerythritol tetranitrate) contained within a waterproofed textile covering or a textile and plastic covering, these assemblies for a given length of detonating fuse being only about one-fifth as heavy as the same length of "Cordeau." Commercially available forms of this detonating fuse are well known. They have much greater tensile strength than "Cordeau" fuse, better resistance to deformation, are relatively easy to handle and use, and have a higher velocity of detonation and better priming power. At a considerable increase in cost, detonating fuse having even higher tensile strength can be obtained by applying metal wire wrapping over the fabric covering. The flexibility of the fabric-covered cord, however, is inadequate for satisfactory use at temperatures below about —40° F., and the flexibility is even further impaired by the presence of reinforcing wire coverings. Although PETN, the explosive core, is not soluble in water and absorbs water very slowly, the above described fabric-covered, PETN-containing, detonating fuse is not completely waterproof; for example, wet ends may lead to priming failures, and failure of propagation of detonation to branch lines may occur if water penetrates at knotted connections where the waterproofing cover is broken. Furthermore, knotted connections may cause failures of propagation unless the branch line is at an angle greater than about 30° from the main line in the direction of detonation.

Flexible detonating compositions, as well as shaped articles containing such compositions, also have become available in recent years in the form of sheets, cords, and

other shaped masses as disclosed in U.S. Patent Nos. 2,992,087, 2,999,743, 2,965,466, 2,999,744, 3,018,201, and 3,116,186. These detonating compositions generally comprise a cap-sensitive explosive held in a matrix of one of several polymeric binders, incorporation of which requires exothermic fluid polymerization, relatively high temperature curing, or incorporation in volatile, toxic or flammable solvents which subsequently are removed; all processes which are unattractive from the standpoint of safety in manufacture, and generally give products which lack flexibility at low or subzero temperatures, or have limited toughness at ordinary temperatures, said toughness being further reduced at elevated temperature. These deficiencies in physical properties are especially apparent, for example, in the ease with which the compositions are cut through by reinforcing members under tension, in the significant loss of tensile strength as temperatures of the compositions increase from room temperature to 140° F. or even higher, and in the brittleness which is apparent at temperatures of 0° F. and lower. The manufacturing procedures employed and some of the binders used in the explosive compositions are inherently expensive to the point of resulting in flexible products whose limited special properties are attained only at a considerable economic penalty.

The potential utility of shaped explosive articles comprising particulate cap-sensitive detonating explosives in a natural or synthetic rubber matrix was disclosed in U.S. Patent 2,067,213, and methods of manufacturing the compositions by incorporating the cap-sensitive high explosives in water-bearing rubber latices also were disclosed. Such compositions and the articles made from them, however, were not suitable for general use over the wide range of temperatures encountered under normal conditions of use in the explosive industry because the articles lost their flexibility and became stiff and brittle at relatively low temperatures, of the order of 0° F., and lacked sufficient tensile strength for satisfactory use at the higher end of the temperature range, e.g., about 120° F. As a result, detonating tapes, sheets, cords and trains made from such compositions were not generally adopted for use in the industry.

An object of this invention is to provide novel explosive compositions. A further object of the invention is to provide explosive compositions that are flexible. Another object of the invention is to provide a novel detonating fuse that has superior properties of flexibility and tensile strength over a wide temperature range. Another object of the invention is to provide a commercially feasible and economical method for making explosive compositions and also for fabricating the compositions into various shapes for subsequent use.

It has now been discovered that novel explosive compositions are obtained by intimately mixing a polymeric carboxylic elastomer that is a copolymer of from about 50 to 80 percent by weight of a butadiene, from about 10 to 45 percent by weight of an acrylonitrile and a sufficient amount of an acrylic acid to provide from about 0.001 to 0.3 carboxyl equivalents per 100 parts by weight of said copolymer; a source of polyvalent metal ions in an amount chemically equivalent to about 0.5 to 2 times the carboxyl content of the copolymer; from about 1 to 20 percent by weight of a plasticizer; and

from about 40 to 80 percent by weight of a particulate cap-sensitive high explosive. Preferably, but optionally, up to 25 percent by weight of a liquid polyurethane elastomer is added to the explosive composition in order to obtain optimum physical properties in relation to flexibility.

Thus, the novel elastomer-bonded explosive composition of the present invention comprises an intimate uniform mixture of from about 40 to 80 percent by weight of a cap-sensitive particulate high explosive, from about 15 to 50 percent by weight of a polymeric metallocarboxylate elastomer and from about 1 to 20 percent by weight of a plasticizer for the carboxylate elastomer. The polymeric metallocarboxylate elastomer is the reaction product of a polyvalent metal ion, which acts as a curing agent for the elastomer, with a copolymer of from about 50 to 80 percent by weight of a butadiene, from about 10 to 45 percent by weight of an acrylonitrile and a sufficient amount of an acrylic acid to provide from about 0.001 to 0.3 carboxyl equivalents per 100 parts of said copolymer, the polyvalent metal ion being present in an amount chemically equivalent to about 0.5 to 2 times the carboxyl content of said copolymer. Most preferably, the explosive composition contains up to about 25 percent by weight of a polyurethane elastomer. However, the amount of polyurethane, if used, should generally not exceed about the amount of metallocarboxylate elastomer.

The resultant explosive composition is flexible and can be formed into a variety of shapes that retain substantially the dimensions and form into which the compositions are fabricated. For example, the explosive compositions can be shaped by pressing into blocks, slabs or sheets, by rolling into sheets and films, and by extruding into rods, cords, tubes or sheets. The shaped articles are flexible, yet have a desirable high tensile strength. These explosive compositions have been found to be particularly useful and supply a long sought after need in the explosive industry, especially when formed into tubes, tapes and cords which can be produced by, for example, continuous rolling or extrusion operations. It has been found that explosive cord, or as it is more commonly referred to in the industry, detonating fuse, fabricated from the novel explosive compositions, and preferably, but not necessarily, containing a reinforcing element and a polyurethane elastomer, greatly increases the uses and conditions under which detonating fuse operates effectively. For example, flexibility and strength of the detonating fuse of this invention are retained to such an extent that the compositions and articles of the invention are useful over a temperature range of from about −50° F. to 180° F.

In relation to detonating fuse, any reinforcing element that is compatible with the explosive composition can be used. Optimum physical properties as to flexibility and tensile strength are obtained when the explosive composition is formed into an elongated or cord-shaped fuse, and yarn, particularly nylon yarn, is employed as the reinforcing element which is substantially centrally positioned within the fuse and along its longitudinal axis.

In order to more fully describe a preferred embodiment of a detonating fuse and its method of preparation, reference is made to the single figure in the drawing illustrating one means for manufacturing detonating fuse.

The drawing illustrates a cross sectional view of an apparatus for extruding the explosive composition around a central reinforcing member in order to make a reinforced detonating fuse, which is a preferred embodiment of the invention. The apparatus comprises a ram type extruder **10** and a barrel **12**, a ram **11** at one end of extruder **10** and a forming means comprising a die **15** at the other end of the extruder. The carboxylate elastomer-containing explosive **18** is added to barrer **12** of extruder **10**. Reinforcing means **17**, e.g., nylon yarn is fed from a source, not shown, into a channel in guide member **13**, through guide insert **14** into the explosive composition. In operation, when pressure is applied to the ram **11**, provided with "O" type sealing rings **16**, it thus forces the explosive composition through die **15** while the reinforcing element is simultaneously fed through guide **13** and guide insert **14** at a predetermined synchronized rate into the explosive composition thus forming detonating fuse **19**. The detonating fuse may be wound on a spool, or other suitable means, for storage.

After the detonating fuse has been formed, e.g., extruded, it is cured. Curing is merely the completion of the reaction between the polyvalent metal ion and the carboxylic elastomer and can take place at room temperature during storage. However, heating the detonating fuse at temperatures below the decomposition temperature of the particulate cap-sensitive high explosive greatly reduces the curing time. A convenient curing temperature being of the order of 160° to 225° F. and from about 8 to 24 hours.

High explosives suitable for use in the present invention include particulate cap-sensitive materials which are stable under the processing conditions, which are compatible with other ingredients of the compositions, and which are not dissolved by other components of the mixtures. The cap-sensitive particulate high explosive constitutes 40 to 80 percent by weight of the explosive composition. Representative cap-sensitive high explosives that can be used are trinitrotoluene (TNT), pentaerythritol tetranitrate (PETN), trinitrophenyl methylnitramine (tetryl), cyclotrimethylenetrinitramine (RDX), cyclotetramethylenetetranitramine (HMX), mannitol hexanitrate, tetranitrodibenzo-1,3a,4,6a-tetraasapentalene, diazidodinitrophenol, hexamethylene triperoxydiamine, picrylsulfone, potassium dinitroacetonitrile, and lead azide. PETN, tetryl, and RDX are the preferred cap-sensitive explosives of the composition, and especially preferred for general use is PETN. The particle size of the high explosive is not critical to the success of the invention, although particles all of which pass an 80-mesh U.S. standard sieve are preferred, and especially preferred are particles whose major dimensions on the average does not exceed 100 microns. The latter are designated herein as superfine explosives. Generally, the compositions are more sensitive to initiation if they contain a very fine crystalline cap-sensitive explosive. The particulate, cap-sensitive high explosive may be dry when added for incorporation into the mixture or it may be wet with water, since water is a major component in the latex of the reaction mixture. Use of water-wet high explosive adds to safety in the manufacturing operation since the water acts as a desensitizer until the explosive is thoroughly incorporated with the carboxylic elastomer and plasticizer, after which the water is removed, for example, by heat and vacuum.

Any plasticizer for the carboxylic copolymer of the explosive composition can be used. Incorporating from about 1 to 20 percent plasticizer by weight assists in providing low temperature flexibility for the explosive composition. Plasticizers which are particularly suitable for use either alone or in combination in said compositions are esters and include, for example, triethyleneglycol-di-2-ethylhexoate, di-n-butyl phthalate, tricresyl phosphate, acetyl tributyl citrate, isodecyloctylphthalate, di-isodecyl adipate, di-isooctyl adipate, dioctyl adipate, dioctyl sebacate. Particularly preferred plasticizers are di-n-butyl phthalate and triethyleneglycol di-2-ethylhexoate which may be used either alone or in combination. Other plasticizers which may be used include, for example, di(butoxyethoxyethyl)formal, tris(β - chloroethyl) - phosphate, and highly aromatic oils such as "Mobilsol" N, "Picco" 25, and "Dutrex" 1739. Preferably these will be used in combination with one of the organic ester type plasticizers named above.

Carboxylic elastomers which are suitable for manufacture of compositions and articles of this invention and constitute the major portion of the binding matrix thereof

are copolymers formed from a butadiene-1,3-hydrocarbon, an acrylic nitrile, and an acrylic acid. Typical butadiene-1-3-hydrocarbons used in preparing said copolymers are, for example, butadiene-1,3 and the 5 to 9 carbon atom homologues thereof such as isoprene, 2,3-dimethyl butadiene-1,3,pentanediene-1,3,hexadiene - 1,3 and mixtures thereof. As used herein, the term "acrylic nitrile" refers to acrylonitrile and alpha-substituted acrylonitriles, that is, compounds having the formula:

$$CH_2=\underset{|}{C}-CN$$

Examples of acrylic nitriles are acrylonitrile, methacrylonite, ethacrylonitrile, alpha-butylacrylonitrile, alpha-phenyl acrylonitrile, alpha-chloroacrylonitrile and alpha-methoxymethyl acrylonitrile and mixtures thereof.

Carboxyl groups are introduced into the copolymers by copolymerizing the aforementioned butadiene-1,3-hydrocarbons and acrylic nitriles with at least one acrylic acid. Copolymers containing about from 0.001 to 0.3, and preferably 0.02 to 0.15, carboxyl equivalent of at least one acrylic acid per 100 parts by weight of copolymer are preferred. As used herein the term "carboxyl equivalent" of an acrylic acid refers to the amount of the chemically combined acrylic acid which contains one equivalent weight, that is, 45 parts by weight of free carboxyl groups. The amount of free carboxyl groups in a given copolymer can be determined by titrating a solution of the carboxylic-modified copolymer with alcoholic potassium hydroxide to a phenolphthalein end-point. As used herein, the term "acrylic acid" refers to acrylic acid and alpha-substituted acrylic acids, that is, compounds having the structural formula:

$$CH_2=\underset{|}{C}-COOH$$

Acrylic acids which are copolymerized with butadiene-1, 3-hydrocarbons and acrylic nitriles thereby introducing free carboxyl groups into the copolymers are, for example, acrylic acid, methacrylic acid, ethacrylic acid and alpha-chloro acrylic acid. Copolymers of from 50 to 80% by weight of a butadiene and from about 10 to 45% by weight of an acrylonitrile containing from about 0.001 to 0.3, and especially 0.02 to 0.15, carboxyl equivalent of an acrylic acid per 100 parts by weight of copolymer are preferred. Especially preferred carboxylic copolymers for use in making articles of the present invention are made from butadiene-1,3, acrylonitrile, and methacrylic acid.

Although said copolymers may be incorporated into the explosive composition by first dispersing them in volatile organic solvents such as aliphatic hydrocarbons, halogenated aliphatic hydrocarbons, toluene, or methyl ethyl ketone, the preferred form of the copolymers is a latex containing from about 35–60% of solids dispersed in an aqueous medium. Such latices present several advantages since latices are the form in which said copolymers are made and, therefore, represent the lowest cost form of the copolymers; no costly and hazardous organic solvents are required to fabricate the articles of this invention; and finally the presence of water in the latex greatly increases the safety of mixing operations wherein a cap-sensitive particulate high explosive is incorporated with the copolymer, the plasticizer, and the source of polyvalent metallic ion. During mixing the reaction mixture may be heated to slowly remove the water or solvent.

Several grades of said butadiene-1,3, acrylonitrile, methacrylic acid copolymers may be made, depending upon the ratios of the monomeric molecules which are incorporated in the copolymer. Generally these are described as high, medium, or low acrylonitrile copolymers depending on the proportion of acrylonitrile incorporated in the copolymer, e.g., 50–35%, 35–17%, and 17–1%, respectively for high, medium, and low; and are further characterized by the carboxyl content of the copolymer, as indicated above. For manufacture of articles of the present invention, latices of copolymers of intermediate acrylonitrile content, and carboxyl (—COOH) content of 0.02 to 0.15 parts by weight per 100 parts of copolymer, are preferred. Such latices are commercially available as, for example, Hycar® 1570X20, 1570X36, 1571 and 1572 (made by the B. F. Goodrich Chemical Co.), of which Hycar® 1572 is especially suitable. Such commercially available copolymer latices may be used alone, or in combination with one another or in combination with polyurethane elastomers in order to obtain the physical properties desired in the finished compositions. Adjustments of compositions, curing agents and processing conditions to obtain desired physical properties is well known in elastomer technology and is regularly practiced by those familiar with elastomer art.

Any source of polyvalent metal ions can be used as a curing agent for the carboxylic copolymer. Polyvalent metal oxides, hydroxides and other sources of polyvalent metal ions such as salts of an acid weaker than acetic acid, and salts of an acid readily eliminated from the cross-linking site, and even finely divided metals, are compounded with, and are used to cure, said carboxylic copolymers by forming corresponding metallocarboxylate. Representative examples of such metal oxides and other sources of polyvalent metal ions are, for example, zinc oxide, calcium oxide, magnesium oxide, dibutyltin oxide, lead oxide, barium oxide, cobalt oxide, tin oxide, zinc carbonate, calcium silicate, zinc acetate, sodium aluminate, sodium phosphomolybdate, and mixtures thereof. Zinc oxide is preferred. Usually from about 0.5 to 2 times the chemical equivalent weight of polyvalent metallic oxide, or other source of polyvalent metal ion, with respect to the amount of carboxyl group in said carboxylic copolymer is used in formulating compositions and articles of this invention.

It can be seen from the above that the metallocarboxylate is the reaction product, formed in situ, between a polyvalent metal ion and a carboxylic copolymer of a butadiene, an acrylonitrile, and an acrylic acid, said copolymer containing from 0.001 to 0.3 carboxyl equivalents of an acrylic acid for each 100 parts by weight of copolymer, and constitutes 15 to 50% by weight of the explosive composition. At least about 15% of the polymeric metallocarboxylate is required to give the desired flexibility, abrasion resistance, and tensile strength to the compositions, but if more than about 50% of said metallocarboxylate is present, the sensitivity of the explosive composition may be less than is desired for effective initiation and propagation of detonation, especially in articles of small cross section or diameter, or across joints between articles. The carboxylic copolymers which are used in the compositions, and their methods of preparation are described in detail, for example, in U.S. Patent Nos. 2,395,017 and 2,724,707 and are further described in "A New High-Strength Elastomer," Rubber World, 130, 784–8 (1954); "Carboxylic Elastomers," Industrial and Engineering Chemistry, 47, 1006–12 (1955); and Rubber Chemistry and Technology, 28, 937 (1955).

Preferably, up to about 25 percent by weight of a polyurethane elastomer, either a polyether or linear polyester type, is incorporated in the explosive composition. The addition of a polyurethane elastomer is especially desirable in explosive compositions which are to be shaped into detonating fuse. Liquid polyurethane elastomers which are characterized by having reactive isocyanate groups by which said liquid polymers can be cured to form solid elastomers, as is well known in the art pertaining to synthetic elastomers, are particularly suitable and are commercially available as, for example, Adiprenes® L–100, L–167, L–315, and L–420 which are manufactured by E. I. du Pont de Nemours & Co.

Adiprene® L–100 is a liquid polyether urethane elastomer which is made by reacting 1 mol of polytetramethylene ether glycol (PTMEG) of number average molecular weight about 1000 with about 1.6 mols of mixed

tolylene diisocyanates, as disclosed, for example, in U.S. Patent Nos. 2,929,800 or 2,948,691. Adiprene® L–315 also is a liquid polyether urethane elastomer and is made by reacting 1 mol of PTMEG of number average molecular weight about 1000, 1 mol of butanediol-1,3 and about 4 mols of mixed tolylene diisocyanate isomers for 4 hours at 80° C. under nitrogen, as disclosed in U.S. Patent No. 3,188,302. Such liquid polyether urethane elastomers sometimes are designated as prepolymers or intermediate polymers because on reaction with curing agents they are cured or vulcanized to form solid elastomers.

Liquid polyurethane elastomers, even when incorporated into compositions of the invention without added curing agents, do cure to some extent and enhance the toughness of the final explosive composition. Preferably, however, curing agents for the liquid polyurethane elastomers also are included in the formulation, as exemplified hereinafter. Said curing agents include diamines, polyols, titanate esters, and others well known in the art. Diamines are the best general purpose curing agents, and 4,4'-methylenebis(2-chloroaniline), commonly designated MOCA®, is preferred. By reaction with said diamine, for example, the liquid polyurethane elastomer is converted to a cured solid polyurethane elastomer which forms a part of the rubbery binder matrix of the explosive compositions and articles of the invention.

The designated carboxylic elastomers and polyurethane elastomers are especially suitable for the preparation of shaped articles, e.g., detonating fuse, of the present invention because these polymers can be crosslinked, i.e., vulcanized or cured, at temperatures much lower than those employed with other elastomers. Curing may be achieved even at room temperature, but preferably is accomplished in a shorter time at elevated temperatures. The temperature chosen will be regulated by the thermal stability of the explosive-containing mixture which is being cured, and, of course, curing temperatures are less than the thermal decomposition temperature of the cap-sensitive explosive. Thus, for example, a temperature of 200–225° F. is convenient for curing PETN-containing compositions. A further advantage associated with use of said elastomers in the products and process of the present invention is that the commonly used sulfur and sulfur-bearing accelerators are not required to cure the initially plastic rubbery mixture. Sulfur and sulfur-bearing vulcanization accelerators are incompatible with many cap-sensitive explosives, i.e., degradative chemical reactions may take place at elevated temperatures of processing and storage. Thus, the advantages of good cure at relatively low temperatures, freedom from the requirement of milling which is standard practice with conventional curable elastomeric materials, and elimination of sulfur and sulfur-bearing curing agents are highly desirable for high explosives-containing compositions, as in the present invention, and are characteristic of elastomers employed in the practice of this invention.

It will be understood that small amounts of other ingredients, if desired, may be incorporated in the explosive compositions of this invention; for example, stabilizers, pigments and coloring agents for identification or for increasing visibility, odorants to create a pleasant aroma or overcome an objectionable odor of the cured elastomeric binder matrix, antioxidants and retardants.

Useful shaped articles may be formed from the explosive compositions of this invention as hereinbefore described, without incorporating reinforcing means, and the scope of the invention should be understood to include such articles. For example, the explosive compositions in an uncured or partially cured state may be shaped into blocks, slabs, tubes, sheets, cords, strips or trains and other forms and finish-cured at room or elevated temperatures. Such explosive articles are elastically extensible and find many uses in the explosive field, but their utility is greatly increased by including in the article a reinforcing means bound to the explosive composition in such manner as to provide an article having great flexibility, even at subzero temperatures, little extensibility, and much greater tensile strength than in the absence of such reinforcing means.

The compositions and articles of the present invention, whether they include a reinforcing means or not, are particularly effective and have a high order of utility in the explosives industry because said explosive compositions and articles made therefrom are surprisingly insensitive to impact and mechanical abuse, they remain completely effective after long exposure to water, they require no supplementary protective covering for handling, they are nontoxic to users, and in comparison with other explosive compositions used in the industry they have enhanced initiating or priming power because of the high concentration of explosive at the initiation point and the freedom from inert layers of protective covering between initiator and receptor bodies.

Any reinforcing element can be used in the detonating fuse but yarns and threads are preferred. Yarns which are suitable for use as reinforcing means in the detonating fuse will be selected in accordance with the strength and performance requirements of the fuse. Such yarns may be made of cotton, linen, jute, silk, wool, rayon—especially high tenacity rayon, cellulose esters, nylon, poly(ethylene terephthalate), polyacrylonitrile, glass or other fibers. Spun fiber yarn construction usually is preferred to simple monofilament threads since a better bond is established between the spun yarn and the explosive composition of the invention. Especially preferred reinforcing means are textured and multiplex yarns more specifically described below. It is believed that the strength of the bond between the explosive composition and the reinforcing means represents a combination of adhesive and mechanical interlocking forces.

Completely satisfactory bond strength is attained when the tensile strength of the article equals or exceeds the tensile strength of the reinforcing means. That is, a sleeve of the explosive composition in the articles of the present invention will not strip free of the reinforcing means when tension is applied between a portion, for example 12 inches, of the article and exposed extensions of the reinforcing means. Yarns which are especially suitable as reinforcing means in the fuse, for example, a column of said explosive composition containing a central yarn strand or a multiplicity of yarn strands as the reinforcing means, are textured yarns as described in U.S. Patent No. 2,783,609 and multiplex yarns as disclosed in copending and coassigned patent application of Field, Ser. No. 397,139, filed Sept. 17, 1964. Textured and multiplex yarns are preferred for use as reinforcing means because of the high inherent tensile strength of said yarns and the firm bond which is produced between the yarn and the surrounding sheath of cap-sensitive high explosive composition.

Textured yarn is defined as a bulky yarn comprising a plurality of substantially continuous filaments which are individually convoluted into coils, loops, and whorls at random intervals along their lengths, and characterized by the presence of ring-like loops irregularly spaced along the yarn surface.

A multiplex yarn is defined as a wrapped yarn comprising a core composed of at least two continuous integral core elements of textile fibers and surface wrappings composed of discontinuous textile fibers, the surface fibers being tightly twisted about the core with portions of fibers locked into place in the core, and the core fibers being relatively straight and held together as a compact bundle by the surface wrappings. A multiplex yarn in which the continuous core elements are nylon is especially preferred for use as the reinforcing means in articles of the present invention. The gross tensile strength of said multiplex yarn is conveyed to the shaped articles of this invention because of the strength of binding which is

established between said strand of multiplex yarn and the surrounding detonating explosive composition described herein. For example, use of an 8-ply, 840 denier-per-ply, multiplex nylon yarn as the reinforcing means will result in a detonating fuse having a total diameter of about 0.20 inch and a gross tensile strength in excess of 100 pounds.

For shaped explosive articles in the form of sheets, individual fibers may be dispersed in the plastic rubbery explosive mixture before sheeting out, as by calendering, and curing, or yarns may extend linearly parallel to the long dimension of the sheet. As an alternate, the sheeted explosive composition may be calendered onto one or both sides of a latex-impregnated woven fabric or mesh and cured, said woven fabric or mesh constituting the reinforcing means. Another alternate permits wrapping reinforcing yarns or threads around an extruded cord of said explosive composition, preferably the surface of said cord is coated with the aforementioned latex or liquid urethane polymers, and curing the shaped article. The thread or yarn wrap may be applied as a braided structure over extruded explosive cord which has been precoated wtih the aforementioned latex or liquid urethane polymer, and the whole assembly cured by mild heating. Said woven, wrapped, or braided structure in itself provides the necessary tensile strength for the article, but the bonding of external reinforcing member to explosive core is desirable to prevent the covering from unraveling when the article, a detonating fuse for example, is cut and to prevent the core from slipping out of the external reinforcing means if tension is applied separately to core and cover. Obviously these methods of applying the reinforcing means to the exterior of the shaped explosive composition are much more expensive than the aforementioned high speed extrusion of explosive composition about a central reinforcing member or a group of spaced internal reinforcing member. Hence, the use of internally placed reinforcing means is preferred in articles of the present invention.

Although threads and yarns are preferred as reinforcing means, wire, especially galvanized wire, may be used for this purpose. It is known that the aforementioned elastomeric carboxylic copolymers are strongly adherent to metal and that they can be cured by reaction with free metals, especially metals which provide a polyvalent ion. Prominent among these is zinc. Thus, if some free carboxyl groups are available in the copolymer-bound explosive composition, or the galvanized wire is precoated with said carboxylic elastomer before being covered by said explosive composition, said composition simultaneously cures and adheres to the galvanized iron wire reinforcing member by reaction between the zinc coating on said wire and carboxyl groups of said carboxylic elastomer. On the other hand, urethane polymers are good adhesives between wire and explosive composition even in the absence of specific salt-like chemical bonds.

In one effective embodiment of the present invention, the reinforcing means is impregnated with a carboxylic elastomer, for example a latex of the kind used in making the explosive composition, or a liquid polyether urethane such as, for instance, Adiprene® L–100. Optionally, the elastomer with which yarns, for example, are impregnated may contain plasticizer and curing agents. These promote adhesion between said reinforcing means and the surrounding composition. A firm bond then is established between the reinforcing means and the explosive composition with which it is in contact during the curing period which follows the forming or shaping of said articles.

Whatever construction is employed in making articles of this invention, e.g., detonating fuse, the final step in their manufacture is that of curing the elastomeric binder matrix and simultaneously binding the explosive composition to the reinforcing means. Although curing at room temperature is known, effective cure can be achieved in shorter times by raising the temperature of the article. Curing at elevated temperatures is preferred because much less time is required and because abrasion resistance, toughness, and adhesion to the reinforcing means are all increased. The upper temperature limit for processing, and thereby simultaneously curing the carboxylic copolymer, generally is determined by the thermal stability of the cap-sensitive explosive ingredient in the explosive mixture and thus curing temperatures do not exceed the temperature at which decomposition of the explosive occurs. For example, temperatures of 160–250° F. for 8 to 24 hours are preferred for curing articles containing PETN, but higher temperatures for shorter times, for example 8 minutes at 300° F., may be employed with explosives of greater thermal stability.

The following examples are intended to illustrate the invention further, but not to limit it in any way. Parts and percentages are by weight, unless otherwise specified.

Example 1

Into a a jacketed, kneading-type mixer fitted with a vacuum-tight cover are charged 55 parts of dry superfine PETN (i.e., average particle size of PETN is less than 10 microns in maximum dimension), or water-wet PETN containing 55 parts net of PETN; 59 parts of a carboxylic copolymer latex (Hycar® 1572) containing about 50% solids prepared by aqueous copolymerization of about 71.4% of butadiene-1,3, about 28.5% of acrylonitrile, and 0.07% of methacrylic acid; 8 parts of plasticizer, triethyleneglycol di-2-ethyl-hexoate; 0.5 part of "Agerite White," i.e., di-beta-naphthyl-p-phenylenediamine (an antioxidant); 1.0 part of stearic acid; and 6 parts of ZnO. The order of adding the ingredients is not critical; however, addition of the particulate high explosive last is preferred as a somewhat safer procedure. The cover is placed in position on the mixer, water at about 160° F. is circulated through the mixer jacket, and the agitator is put in motion. After the mixer has operated for about 5 minutes, vacuum gradually is applied, with the agitator in motion, until a vacuum of about 29 inches or more of mercury is achieved, and this is maintained until substantially all water is removed from the charge in the mixer. The use of vacuum is not necessary to complete removal of water or solvent, but its use is preferred because it speeds up processing of the composition. The dried explosive composition is transferred from the mixer to the barrel or charging hopper of a ram-type or screw-type extruder fitted with a cross-head type, circular-orifice die which permits extrusion of the plastic rubbery explosive composition around a multiplex nylon yarn having a gross tensile strength of about 120 pounds as it is drawn through the die. The barrel and die-head of the extruder are held at from about 140° to 170° F. while said composition is being extruded. The multiplex nylon yarn may contain, for example, 8 ends, each of 840 denier, as hereinbefore described, and be preimpregnated with a carboxylic elastomer. The shaped article thereby produced is a partially cured detonating fuse having a central reinforcing means surrounded by a cap-sensitive detonating composition. The detonating fuse as it is continuously extruded may be taken up on a reel, spool, or other storage means. The partially cured fuse is stored at a temperature of from about 200° to 225° F. for about 8 hours when the cure is substantially complete. The fuse has a diameter of about 0.180 inch, is totally unaffected by exposure to water, has a gross tensile strength of about 125 pounds, is easily primed by a commercial blasting cap, and detonates at a velocity of about 6568 meters/sec. (m./s.). The end of a length of primed detonating fuse was attached to and initiated a block of pressed TNT. The flexibility of said detonating fuse was demonstrated by holding the fuse at −50° F. for about one hour and then wrapping said cord around a ¼ in. diameter mandrel without fracturing or cracking the detonating cord. The reinforcing yarn is not stripped from the surrounding detonating composition, even under tension up to rupture, nor does the yarn cut through the explosive composition.

Examples 2 to 6

The table below illustrates additional compositions prepared according to the procedure of Example 1. The percentages represent the composition on a dry basis, as charged to the mixer.

Example	2	3	4	5	6
Explosive	PETN	PETN	PETN	Tetryl	RDX.
Explosive, percent	55	55	55	80	75.
Carboxylic Copolymer	Hycar® 1572	Hycar® 1572	Hycar® 1572 and 1570 x 36.	Hycar® 1572	Hycar® 1572.
Copolymer, percent	33	36	25 and 8	15	20.
Plasticizer	Dibutyl phthalate	Flexol® 3GO [1]	Flexol® 3GO [1]	Flexol® 3GO [1]	Flexol® 3GO [1].
Plasticizer, percent	8	7	8	4.25	4.5.
Curing Agent	ZnO	PbO_2	ZnO	ZnO	ZnO.
Detonation Vel., m./s.	6,350	6,520	6,145	6,000	7,055.
Tensile Strength, [2] lb.	125	125	125	125	125.
Low Temp. Flexibility (¼ in. mandrel) [2]	−50° F.	−50° F.	−50° F.	−20° F.	−20° F.

[1] Flexol® 3GO—triethyleneglycol di-2-ethylhexoate made by Union Carbide Chemicals Co.
[2] Reinforcing member was 8 ply, 840 denier/ply multiplex nylon yarn.
[3] Lower flex temperatures are obtained for detonating cords if a larger diameter mandrel is used in the test.

Example 7

An explosive composition is prepared as in Example 1 and extruded without a central reinforcing means. The extruded fuse after curing has a diameter of about 0.19 inch and has similar properties to the cord of Example 1 except that it is elastically extensible at room temperature and has a gross tensile strength at 68° F. of about 15 pounds at rupture. The unreinforced fuse of this example is flexible at −50° F. when tested as in Example 1.

Example 8

The explosive composition prepared according to this example contains a liquid polyurethane elastomer. This composition, for example, is particularly well suited for fabrication into detonating fuse which is to be knotted, as in joining one piece of detonating fuse to another or to a high explosive primer, and then subjected to a tensile stress, for example, as in lowering an explosive charge into a borehole.

The procedure employed is substantially the same as that described in Example 1, and the ingredients for the composition are:

	Parts
Superfine PETN	58
Hycar® 1572 (50% solids)	48.6
Triethylene glycol di-2-ethylhexoate	8.0
ZnO	5.0
Antioxidant ("Agerite White")	0.5
Liquid urethane polymers, (polyurethane)	3.0
Adiprene® L–100	1.0
Adiprene® L–315	2.0
Methylene-bis(o-chloroaniline) (MOCA®) dissolved in about 7 parts of trichloroethylene	0.7
Dyestuff	0.5

Extrusion and curing of the mixed explosive composition in the form of detonating fuse of circular cross section and having a nylon yarn reinforcing element are carried out as described in Example 1.

Following the teachings of the invention, a novel explosive composition is obtained that is flexible and exhibits excellent tensile strength over a wide temperature range of the order of −50° F. to 180° F. Furthermore, the explosive composition can be formed into a variety of shapes which retain their dimensions under conditions of use; for example, flexible, extensible detonating fuse may be made, with or without a reinforcing means, that is insensitive to impact and effective after exposure to water for an extended period. In addition, the reinforcing means of the detonating fuse remains integrally bound to the explosive composition to prevent any detrimental slippage between said explosive and reinforcing means under differential stress up to the rupture stress of the reinforcing means.

I claim:

1. An explosive composition comprising an intimate uniform mixture of from about 40 to 80 percent by weight of a cap-sensitive particulate high explosive, from about 1 to 20 percent by weight plasticizer, and from about 15 to 50 percent by weight of a polymeric metallocarboxylate elastomer which is the reaction product of a polyvalent metal ion with a copolymer of a butadiene, an acrylic nitrile and an acrylic acid.

2. An explosive composition comprising an intimate uniform mixture of from about 40 to 80 percent by weight of a cap-sensitive particulate high explosive, from about 1 to 20 percent by weight plasticizer, from about 15 to 50 percent by weight of a polymeric metallocarboxylate elastomer which is the reaction product of a polyvalent metal ion with a copolymer of a butadiene, an acrylic nitrile and an acrylic acid, and up to 25 percent by weight of a polyurethane elastomer.

3. An explosive composition comprising an intimate uniform mixture of from about 40 to 80 percent by weight of a cap-sensitive particulate high explosive, from about 1 to 20 percent by weight of a plasticizer, from about 15 to 50 percent by weight of a polymeric metallocarboxylate elastomer which is the reaction product of a polyvalent metal ion with a copolymer of a butadiene, an acrylic nitrile and an acrylic acid, and up to 25 weight percent by weight of a polyurethane elastomer with the proviso that the amount of said urethane does not exceed the amount of said metallocarboxylate elastomer.

4. An explosive composition comprising an intimate uniform mixture of from about 40 to 80 percent by weight of a cap-sensitive particulate high explosive; from about 15 to 50 percent by weight of a polymeric metallocarboxylate elastomer which is the reaction product of a polyvalent metal ion with a copolymer of from about 50 to 80 percent by weight of a butadiene, from about 10 to 45 percent by weight of an acrylic nitrile and a sufficient amount of an acrylic acid to provide from about 0.001 to 0.3 carboxyl equivalents per 100 parts of said copolymer, said polyvalent metal ion being present in an amount chemically equivalent to about 0.5 to 2 times the carboxyl content of said copolymer; and from about 1 to 20 percent by weight plasticizer.

5. An explosive composition comprising an intimate uniform mixture of from about 40 to 80 percent by weight of a cap-sensitive particulate high explosive; from about 15 to 50 percent by weight of a polymeric metallocarboxylate elastomer which is the reaction product of a polyvalent metal ion with a copolymer of from about 50 to 80 percent by weight of a butadiene, from about 10 to 45 percent by weight of an acrylic nitrile and a sufficient amount of an acrylic acid to provide from about 0.001 to 0.3 carboxyl equivalents per 100 parts of said copolymer, said polyvalent metal ion being present in an amount chemically equivalent to about 0.5 to 2 times the carboxyl content of said copolymer; from about 1 to 20 percent by weight plasticizer; and up to about 25 percent by weight of a polyurethane elastomer.

6. An explosive composition comprising an intimate uniform mixture of from about 40 to 80 percent by weight of a cap-sensitive particulate high explosive; from about 15 to 50 percent by weight of a polymeric metallocarboxylate elastomer which is the reaction product of a polyvalent metal ion with a copolymer of from about 50 to 80 percent by weight of a butadiene, from about 10 to 45 percent by weight of an acrylic nitrile and a sufficient amount of an acrylic acid to provide from about 0.001 to 0.3 carboxyl equivalents per 100 parts by weight of said copolymer, said polyvalent ion being present in an amount chemically equivalent to about 0.5 to 2 times the carboxyl content of said copolymer from 1 to 20 percent by weight plasticizer; and up to about 25 percent by weight of a polyurethane elastomer with the proviso that the amount of said urethane does not exceed the amount of said metallocarboxylate elastomer.

7. An explosive composition comprising an intimate uniform mixture of from about 40 to 80 percent by weight of a cap-sensitive particulate high explosive; from about 15 to 50 percent by weight of a polymeric metallocarboxylate elastomer which is the reaction product of a polyvalent metal ion with a copolymer of from about 50 to 80 percent by weight of butadiene, from about 10 to 45 percent by weight of acrylonitrile and a sufficient amount of methacrylic acid to provide from about 0.001 to 0.3 carboxyl equivalents per 100 parts of said copolymer, said polyvalent metal ion being present in an amount chemically equivalent to about 0.5 to 2 times the carboxyl content of said copolymer; from about 1 to 20 percent by weight plasticizer; and up to about 25 percent by weight of a polyurethane elastomer.

8. An explosive composition comprising an intimate uniform mixture of from about 40 to 80 percent by weight of the cap-sensitive particulate high explosive pentaerythritol tetranitrate; from about 15 to 50 percent by weight of a polymeric metallocarboxylate elastomer which is the reaction product of a polyvalent metal ion with a copolymer of from about 50 to 80 percent by weight of butadiene, from about 10 to 45 percent by weight of acrylonitrile and a sufficient amount of methacrylic acid to provide from about 0.001 to 0.3 carboxyl equivalents per 100 parts of said copolymer, said polyvalent metal ion being present in an amount chemically equivalent to about 0.5 to 2 times the carboxyl content of said copolymer; from about 1 to 20 percent by weight plasticizer; and up to about 25 percent by weight of a polyurethane elastomer with the proviso that the amount of said urethane does not exceed the amount of said metallocarboxylate elastomer.

9. An explosive composition comprising an intimate uniform mixture of from about 40 to 80 percent by weight of the cap-sensitive particulate high explosive cyclotrimethylenetrinitramine; from about 15 to 50 percent by weight of a polymeric metallocarboxylate elastomer which is the reaction product of a polyvalent metal ion with a copolymer of from about 50 to 80 percent by weight of butadiene, from about 10 to 45 percent by weight of acrylonitrile and a sufficient amount of methacrylic acid to provide from about 0.001 to 0.3 carboxyl equivalents per 100 parts of said copolymer, said polyvalent metal ion being present in an amount chemically equivalent to about 0.5 to 2 times the carboxyl content of said copolymer; from about 1 to 20 percent by weight plasticizer; and up to about 25 percent by weight of polyurethane elastomer with the proviso that the amount of said urethane does not exceed the amount of said metallocarboxylate elastomer.

10. An explosive composition comprising an intimate uniform mixture of from about 40 to 80 percent by weight of the cap-sensitive particulate high explosive trinitrophenyl methylnitramine; from about 15 to 50 percent by weight of a polymeric metallocarboxylate elastomer which is the reaction product of a polyvalent metal ion with a copolymer of from about 50 to 80 percent by weight of butadiene, from about 10 to 45 percent by

weight of acrylonitrile and a sufficient amount of methacrylic acid to provide from about 0.001 to 0.3 carboxyl equivalents per 100 parts of said copolymer, said polyvalent metal ion being present in an amount chemically equivalent to about 0.5 to 2 times the carboxyl content of said copolymer; from about 1 to 20 percent by weight plasticizer; and up to about 25 percent by weight of polyurethane elastomer with the proviso that the amount of said urethane does not exceed the amount of said metallocarboxylate elastomer.

11. An explosive composition comprising an intimate uniform mixture of from about 40 to 80 percent by weight of the cap-sensitive particulate high explosive pentaerythritol tetranitrate; from about 15 to 50 percent by weight of a polymeric metallocarboxylate elastomer which is the reaction product of the polyvalent metal ion zinc with a copolymer of from about 50 to 80 percent by weight butadiene, from about 10 to 45 percent by weight acrylonitrile and sufficient methacrylic acid to provide from about 0.001 to 0.3 carboxyl equivalents per 100 parts of said copolymer, said zinc ions being present in an amount chemically equivalent to about 0.5 to 2 times the carboxyl content of said copolymer; from about 1 to 20 percent by weight plasticizer; and up to 25 percent by weight of a polyether urethane elastomer with the proviso that the amount of said urethane does not exceed the amount of said metallocarboxylate elastomer.

12. An explosive composition comprising an intimate uniform mixture of the cap-sensitive particulate high explosive pentaerythritol tetranitrate; from about 15 to 50 percent by weight of a polymeric metallocarboxylate elastomer which is the reaction product of the polyvalent metal ion zinc with a copolymer of from about 50 to 80 percent by weight butadiene, from about 10 to 45 percent by weight acrylonitrile and sufficient methacrylic acid to provide from about 0.02 to 0.15 carboxyl equivalents per 100 parts of said copolymer, said zinc ions being present in an amount chemically equivalent to about 0.5 to 2 times the carboxyl content of said copolymer; from about 1 to 20 percent by weight of the plasticizer triethyleneglycol di-2-ethylhexoate; and up to 25 percent by weight of a polyether urethane elastomer with the proviso that the amount of said urethane does not exceed the amount of said metallocarboxylate elastomer.

13. A process for manufacturing an explosive composition which comprises intimately mixing a copolymer which is the reaction product of from about 50 to 80 percent by weight of a butadiene, from about 10 to 45 percent by weight of an acrylic nitrile and a sufficient amount of an acrylic acid to provide from about 0.001 to 0.3 carboxyl equivalents per 100 parts by weight of said copolymer; a source of polyvalent metal ions in an amount chemically equivalent to about 0.5 to 2 times the carboxyl content of the copolymer; from about 1 to 20 percent by weight of a plasticizer; from about 40 to 80 percent by weight of a particulate cap-sensitive high explosive; and drying and curing the explosive composition.

14. A process for manufacturing an explosive composition which comprises intimately mixing a dispersion of a copolymer which is the reaction product of from about 50 to 80 percent by weight of a butadiene, from about 10 to 45 percent by weight of an acrylic nitrile and a sufficient amount of an acrylic acid to provide from about 0.001 to 0.3 carboxyl equivalents per 100 parts by weight of said copolymer; a source of polyvalent metal ions in an amount chemically equivalent to about 0.5 to 2 times the carboxyl content of the copolymer; from 1 to 20 percent by weight of a plasticizer; from about 40 to 80 percent by weight of a particulate cap-sensitive high explosive; up to about 25 percent by weight of a polyurethane elastomer; and drying and curing the explosive composition.

15. A process for the manufacture of an explosive composition which comprises intimately mixing an aqueous dispersion of a copolymer which is the reaction product of from about 50 to 80 percent by weight of a buta-

diene, from about 10 to 45 percent by weight of an acrylic nitrile and a sufficient amount of an acrylic acid to provide from about 0.001 to 0.3 carboxyl equivalents per 100 parts of said copolymer; a source of polyvalent metal ions in an amount chemically equivalent to about 0.5 to 2 times the carboxyl content of said copolymer; 1 to 20 percent by weight of a plasticizer; 40 to 80 percent by weight of a cap-sensitive particulate high explosive; up to about 25 percent by weight of a polyurethane elastomer; removing substantially all the water from the mixture, and curing the explosive composition.

16. The process of claim **15** wherein the cap-sensitive high explosive is cyclotrimethylenetrinitramine.

17. The process of claim **15** wherein the cap-sensitive high explosive is trinitrophenyl methylnitramine.

18. The process of claim **15** wherein the cap-sensitive high explosive is pentaerythritol tetranitrate.

19. A process for the manufacture of an explosive composition which comprises intimately mixing an aqueous dispersion of a copolymer which is the reaction product of from about 50 to 80 percent by weight butadiene, from about 10 to 45 percent by weight acrylonitrile and a sufficient amount of methacrylic acid to provide from about 0.001 to 0.3 carboxyl equivalents per 100 parts of said copolymer; a source of zinc ions in an amount chemically equivalent to about 0.5 to 2 times the carboxyl content of the copolymer; from about 1 to 20 percent by weight of a plasticizer; from about 40 to 80 percent by weight of a cap-sensitive particulate high explosive; up to about 25 percent by weight of a polyether urethane elastomer with the proviso that the amount of said urethane does not exceed the amount of copolymer; removing substantially all the water from the mixture, and curing the explosive composition.

20. The process of claim **19** wherein the cap-sensitive high explosive is pentaerythritol tetranitrate.

21. A process for the manufacture of an explosive composition which comprises intimately mixing an aqueous dispersion of a copolymer which is the reaction product of from about 50 to 80 percent by weight of butadiene, from about 10 to 45 percent by weight of acrylonitrile and a sufficient amount of methacrylic acid to provide from about 0.02 to 0.15 carboxyl equivalents per 100 parts of said copolymer; a source of zinc ions in an amount chemically equivalent to about 0.5 to 2 times the carboxyl content of said copolymer; 1 to 20 percent by weight of a plasticizer; from about 40 to 80 percent by weight of the particulate cap-sensitive high explosive pentaerythritol tetranitrate; up to about 25 percent by weight of polyether urethane elastomer with the proviso that the amount of said urethane does not exceed the amount of said copolymer; removing substantially all the water from the mixture, and curing the explosive composition.

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