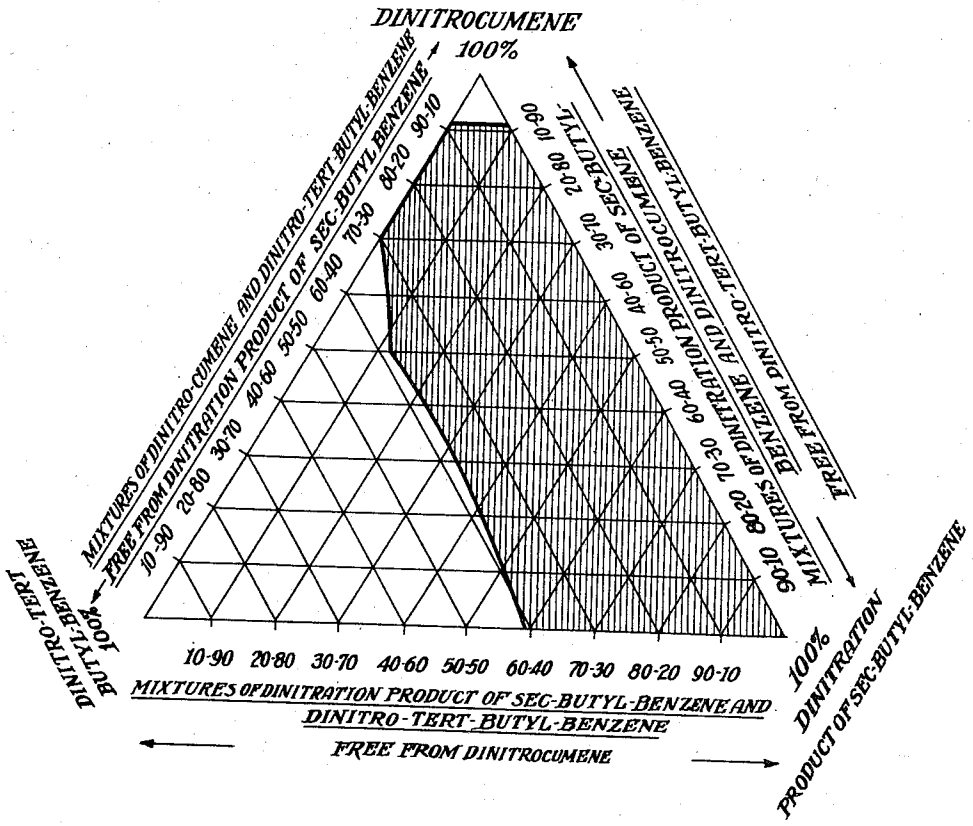
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PLASTIC DETONATING COMPOSITIONS

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PLASTIC DETONATING COMPOSITIONS

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The present invention relates to the production of new or improved plastic or gelatinous detonating explosives for civil or military uses capable or retaining or easily recovering a serviceable consistency even when exposed to low atmospheric temperatures.

Plastic and gelatinous explosives for civil use are based on the use of nitropolyglycerine or mixtures of nitroglycerine with other liquid esters as the self explosive ingredient rendering them sensitive to detonation, and in most of them there is also present a proportion of nitrocellulose gelatinised by the liquid nitric ester.

The inclusion of a proportion of other liquid nitric esters such as nitroglycol or nitroglycerine, and to a lesser extent the inclusion of a proportion of certain aromatic nitrocompounds with the nitroglycerine, has the effect of somewhat reducing the temperature to which a nitroglycerine explosive can be supercooled before it freezes, and low freezing detonating explosives containing a proportion of other liquid nitric esters, frequently accompanied by a proportion of aromatic nitrocompounds, in conjunction with the nitroglycerine are in general use for civil blasting purposes. Liquid nitric ester detonating explosives are, however, frequently too sensitive to initiation by friction and shock for military purposes, even when they are in the unfrozen conditions.

We are aware that a plastic composition freezing with difficulty has already been disclosed, characterised by the fact that the liquid constituent is the mother lye remaining from the crystallisation of a nitro derivative of xylol, cumol or a di or tri nitro derivative of benzol, said liquid constituent being gelatinised with nitrocellulose, in some cases with the addition of nitroglycerine, to which mixture has been added finely pulverised oxygen-yielding or containing substances, such as chlorates, perchlorates, nitrates or the like, and in some cases combustible substances, until a doughy plastic mass is obtained which, similarly to gelatinised dynamite, can be pressed into long plastic strings which may be cut to form cartridges of desired length.

We are also aware that a plastic explosive freezing with difficulty has been disclosed comprising inter alia a gelatine composed of nitrocellulose and a fluid nitro-derivative of a higher homologue of toluene, for instance, a nitro-derivative of xylene or cumene, being a fluid nitro compound of definite chemical constitution, or a plurality of such fluid derivatives, and if desired containing oxygen containing or yielding substances and combustible (carbonaceous) materals.

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In U. S. Patent 2,407,597 there are claimed plastic or gelatinous detonating explosive compositions containing a high explosive solid, for example pentaerythritol tetranitrate, distributed through a matrix comprising nitrocellulose dissolved or gelatinised in a nitro body composition consisting of trinitrotoluene, tetryl and from 70 to 85 per cent by weight of a mixture of dinitrotoluene isomers, which mixture is wholly liquid at 0° C. The pentaerythritol tetranitrate is normally sensitive to initiation by friction and shock, as well as by a detonating impulse, whereas the matrix of nitrocellulose dissolved or gelatinised in the nitro body composition is relatively insensitive to initiation by friction and shock. The plastic or gelatinous explosives of the said pending application are resistant to low temperatures and are of sufficient sensitiveness to a detonating impulse, but of sufficiently low sensitiveness to initiation by friction or shock to enable them to be used for military purposes.

It is however difficult to procure non-volatile liquid aromatic poly-nitrocompound mixtures that will enable the explosive to be stored under cold conditions without the occurrence of crystallisation of the nitrocompound to such an extent that the explosive loses its plastic or gelatinous character and sets irreversibly hard in the sense that the nitro-compounds cannot again be liquified without heating the composition to a temperature considerably above atmospheric.

We have now found it possible however to produce plastic or gelatinous detonating explosives capable of continued storage at low temperature without setting irreversibly hard, wherein a self explosive crystalline solid compound of non-aromatic character is distributed through a continuous matrix comprising compositions liquid at —15° C. making up the shaded portion of the triangular diagram for the multi-component system of dinitration product of secondary butyl-benzene, dinitro-tertiary butyl-benzene and dinitrocumene in the drawing accompanying the specification.

The triangular diagram has been plotted for a temperature of —15° C. and the shaded portion therein is made up of compositions which are free from solid on prolonged storage at this temperature even after seeding with dinitrocumene or dinitro tertiary butyl benzene. The compositions in the unshaded portions however are solid or partially solid at —15° C.

In the diagram the weight percentages of each component are represented by the perpendicular distances from each base to the opposite vertex.

It will be seen that the compositions comprising the hitherto undescribed liquid mixtures of nuclear dinitro-compounds obtainable by direct dinitration of secondary butyl-benzene, if desired in admixture with up to about two thirds its weight of nuclear dinitro tertiary butyl-benzene are represented by the horizontal line forming the base of the shaded area at the right hand corner of the drawing, and that dinitro-cumene may be mixed with the dinitration product of secondary butyl-benzene in amounts up to about 9 times the weight of the latter, whereas the proportion of dinitro tertiary butyl-benzene in the mixture of dinitro-compounds may not exceed about 40%. The introduction of dinitro-cumene enables compositions containing less and less of the dinitration product of secondary butyl-benzene to be used as the proportion of dinitro-cumene is increased, so that a limited range of compositions free from the dinitration product of secondary butyl-benzene can even be employed.

A thickening agent of colloidal character is preferably present in the matrix in solution in the mixture of dinitro-compounds in order to render it viscous or gelatinous and to assist in preventing exudation. Nitrocellulose or other cellulose esters or the like may be used for this purpose.

Other solid undissolved ingredients usual in explosive compositions may be present in addition to the aforesaid crystalline solid self explosive compound distributed through matrix but these should not include solid aromatic compounds unless they are insoluble in the aforesaid dinitro-compounds or mixture of dinitro-compounds. For instance explosive salts such as ammonium nitrate, oxidising salts, porous absorbents, flame quenching ingredients, oxidisable ingredients and the like may be included.

The non-aromatic crystalline solid self explosive compound distributed through the matrix may advantageously be a nitric ester, for example pentaerythritol tetranitrate or hexanitromannitol, or a nitramine, for example cyclotrimethylene-trinitramine.

By dinitro-cumene we mean the liquid mixture of isomers solidifying about +8° C. that may be prepared from cumene by the conventional processes employed for the conversion of aromatic-hydrocarbons substantially wholly into their dinitro-derivatives by means of nitric and sulphuric acids in association. The nitration is conveniently conducted in two stages, using a stronger acid mixture for the conversion of the mono-nitrated hydrocarbon into the dinitrated hydrocarbon than for the production of the mono-nitrated-hydrocarbon in order to minimise the amount of tri-nitration.

The di-nitration product of secondary butyl-benzene may be similarly prepared from secondary butyl-benzene, and is a liquid at temperatures down to about −5° C., which deposits only an unimportant percentage of a solid when it is subjected to prolonged storage at −15° C. On further cooling to about −25° there is little further deposition of solid. The isomers constituting the liquid mixture are new compounds in which both the nitro-groups are nuclearly positioned, but they have not yet been separated, enumerated and individually characterised by their constitutions. Dinitro tertiary butyl-benzene, which may be prepared similarly, is a solid melting at 62° C., and is generally understood to be a single compound. It has a tendency to supercool, and a lower melting point is frequently observed until a number of preparations of the solid have been made in the same surroundings.

The dinitro-cumene, and the dinitration product of secondary butyl-benzene or the dinitro-tertiary butyl-benzene, or all three, may be separately produced from the corresponding aromatic hydrocarbons or from mono-nitration products of these, and then mixed; or the mono-nitration products may be prepared from the separate aromatic hydrocarbons and may be mixed and subjected to a further stage of nitration. For the purpose of forming the mixture of dinitration products, however, it is usually most convenient to subject a previously formed mixture of the un-nitrated aromatic hydrocarbons in the required proportions to dinitration, preferably in two stages as aforesaid. The mixed nitrating acid is preferably run into the mixture of mono-nitrated hydrocarbons, in order to minimise the amount of tri-nitration. It is then unnecessary to purify the mixture from tri-nitro-hydrocarbons. Mixtures consisting mainly of secondary and tertiary butyl-benzenes are available industrially, and fractions of suitable compositions for admixture with cumene, which is also an industrially available product, can be distilled from these.

A method applicable to the production of dinitro-cumene that is also applicable to the production of the dinitration product of secondary butyl-benzene, or to mixtures of dinitro-cumene with the dinitration product of secondary butyl-benzene or with dinitro-tertiary butyl-benzene, or with both, from the corresponding aromatic hydrocarbons or hydrocarbon mixture is as follows:

The mono-nitration is conducted by adding gradually 0.9 part cumene (or 1 part of the butyl-benzene) with stirring to 3 parts by weight of a mixed acid containing 55% sulphuric acid, 25% nitric acid and 20% water, originally warmed to about 30° C. The contents of the nitrating vessel are allowed to rise in temperature to about 40° C. during the addition of the mixed acid and thereafter to 50° C. at which temperature stirring is continued for half an hour. The mixture is diluted with a small amount of water, and the yield of the mono-nitrated product is about 98% theoretical. The top layer consisting of the acid-wet mono-nitrated product is placed in a nitrator and warmed to about 40° C., thereupon twice its weight of a mixed acid of the composition sulphuric acid 70%, nitric acid 24% water 6% is gradually run into the nitrator with stirring. The temperature is allowed to rise during the addition, and stirring continued at that temperature for one and a half hours. The product is then separated and washed with a small amount of water, in which it sinks, and then with a faintly alkaline solution such as an alkaline carbonate or sulphite to remove the last traces of acid. It is then dried at raised temperature, advantageously by passing a current of air through it.

If desired, we can prepare the plastic or gelatinous detonating explosives of the present invention according to the process claimed in co-pending application Serial No. 549,639 which claims inter alia forming a slurry of a finely crystalline high explosive compound sensitive to detonation by friction or shock and nitrocellulose in a substantial quantity of cold water, mixing into the said slurry at ordinary temperatures at least one substantially non-volatile and rela-

tively sensitive to friction or shock water insoluble liquid solvent for nitrocellulose insufficient to form a continuous phase but sufficient to agglomerate the nitrocellulose and crystals into discrete aggregates each containing the said nitrocellulose in swollen but incompletely gelatinised condition associated with said solvent and a plurality of said crystals, separating the still discrete aggregates from the bulk of the cold water without the application of any appreciable pressure, and drying the separated aggregates without causing any substantial coalescence thereof.

The following examples illustrate military explosives provided according to the invention:

Example 1

The ingredients are as follows:	Per cent
Pentaerythritol tetranitrate	66
Dinitro-secondary butyl benzene	30
Quarter second industrial nitrocellulose of 11.9% nitrogen content	3.6
Blasting soluble nitrocellulose	0.4

The pentaerythritol tetranitrate and the nitrocellulose used in the water wet condition and mixed together with half the dinitro-secondary butyl-benzene under water, the resulting granules being dried off in an oven and mixed with the other half of the dinitro-secondary butyl-benzene in a McRoberts mixer. The plastic explosive has a power of about 84% that of blasting gelatine, a velocity of detonation of 7000 metres per second and is capable of initiation by a No. 6 lead azide detonator. On storage at −15° C. it shows some change in consistency, but the nitrocompounds do not crystallise out. It becomes plastic again when further stored at a temperature of about −5° C.

Example 2

The proportions of pentaerythritol tetranitrate and nitrocellulose are the same as in Example 1. In place of the dinitration product of secondary butyl-benzene there is used 30% of a mixture of dinitro-secondary butyl-benzene and dinitro-tertiary butyl-benzene in the ratio 75:25. The explosive is made in the manner described in Example 1 and has similar properties except that it can be stored without setting irreversibly hard at an even lower temperature than that described in Example 1.

Example 3

The ingredients are the same as in Example 1 except that in the place of the dinitro-secondary butyl-benzene there is used 30% of a mixture of dinitro-secondary butyl-benzene and dinitro-tertiary butyl-benzene in the ratio 45:55. The explosive is made in the manner described in Example 1, and has similar properties except that it cannot be stored at quite so low temperatures without setting irreversibly hard.

Notwithstanding the fact that these mixtures of dinitro-secondary butyl-benzene and dinitro-tertiary butyl-benzene deposit some solid crystalline matter at temperatures above +10° C. this explosive does not go irreversibly hard when stored at −10° C. and recovers its plastic consistency at a temperature below 0° C.

Example 4

The ingredients are the same as in Example 1, except that the pentaerythritol tetranitrate is replaced by cyclotrimethylene-trinitramine; the process is otherwise the same as described in Example 1. The resulting explosive is likewise of high power and velocity and is capable of initiation by a No. 6 lead azide detonator. On storage at −15° C. it shows some change in consistency but does not set irreversibly hard.

Example 5

The ingredients were as follows:	Per cent
Pentaerythritol tetranitrate	67.1
Mixture containing 50% dinitrocumene, 12½% dinitro secondary butyl-benzene and 37½% dinitro tertiary butyl-benzene	29½
Thirty-five second industrial nitrocellulose of 11.9% nitrogen content	3.0
Blasting Soluble Nitrocellulose	0.4

Blasting soluble nitrocellulose is the product of nitration of purified cotton cops by the pot process to a nitrogen content of 11.95 to 12.25%. The product is at least 95% soluble in an ether-alcohol solution, and has a viscosity of 100 to 300 c. g. s. in solution of 3 gms. in 100 ml. acetone (95%) at 20° C.

The mixture containing the dinitro-cumene, the dinitro secondary butyl-benzene and the dinitro-tertiary butyl-benzene was obtained by nitration in two stages of a mixture of equal weights of cumene and a distillate amounting to 80% of the amount of a commercially available mixture consisting mostly of secondary and tertiary butyl-benzene, the ratio of the amounts of tertiary and secondary hydro-carbons in the distillate being 3:1.

The pentaerythritol tetranitrate and the nitrocellulose were used in the water wet condition and were mixed together with half the dinitro aromatic hydrocarbon mixture under water, the resulting granules being dried off in an oven and mixed with the other half of the dinitro aromatic hydrocarbon mixture in a McRoberts mixer. The explosive had a power of about 86% of that of blasting gelatine and a velocity of detonation of about 7,000 metres per second, and it was capable of initiation by a No. 6 lead azide detonator. On storage at −14° C. it showed some change in consistency, but the nitro compounds did not crystallise out and the explosive readily assumed its plastic condition when it was further stored at a temperature of about 0° C.

Example 6

The proportions of pentaerythritol tetranitrate and of the nitrocellulose were the same as in Example 5. A mixture of dinitro-cumene and dinitro secondary butyl-benzene in the ratio 50:50 prepared by dinitration from a mixture of cumene and secondary butyl-benzene was used. The properties of the explosive were not very different from that of the explosive described in Example 5.

Example 7

The proportions of pentaerythritol tetranitrate and of the nitrocelluloses were the same as in Example 6. A mixture of dinitro-cumene, dinitro secondary butyl-benzene and dinitro tertiary butyl-benzene in the ratio 90:5:5 was used, this mixture being prepared by nitration in two stages from a mixture of cumene, secondary butyl-benzene and tertiary butyl-benzene in these proportions. The method by which the ingredients of the explosive composition were mixed was the same as in Examples 5 and 6. The properties of the explosive were not very different from those of the explosive prepared in Example 6.

Example 8

The proportions of pentaerythritol tetranitrate and of the nitrocelluloses were the same as in Example 6. A mixture of dinitro-cumene and dinitro tertiary butyl-benzene in the ratio 70:30 was used, this mixture being prepared by nitration in two stages from a mixture of cumene and tertiary butyl benzene in these proportions. The method by which the ingredients of the explosive composition were mixed was the same as in Example 5. The properties of the explosives were not very different from those of the explosive prepared according to Example 5.

Example 9

The ingredients are the same as in Example 5, except that the pentaerythritol tetranitrate is replaced by cyclo-trimethylene-trinitramine. The process by which the explosive is made is otherwise the same as that described in Example 5. The resulting explosive is likewise of high power and velocity and is capable of initiation by a Number 6 lead azide detonator. On storage at —14° it showed some change in consistency, but the aromatic nitro-compounds did not crystallise out, and the explosive readily resumed its plastic condition when it was further stored at a temperature of about 0° C.

We claim:

1. Plastic detonating explosives capable of being stored continuously at low temperatures without setting irreversibly hard which comprise a self-explosive solid compound from the group consisting of self-explosive non-aromatic crystalline solid nitric esters and cyclo-trimethylene-trinitramine distributed through a continuous matrix comprising a liquid which freezes below —15° C. and the composition of which is shown in the shaded portion of the triangular diagram for the multi-component system of dinitro-cumene, dinitro tertiary-butylbenzene and the dinitration product of secondary-butylbenzene in the drawing accompanying the specification.

2. Plastic detonating explosives as defined in claim 1 wherein the self-explosive solid compound is pentaerythritol tetranitrate.

3. Plastic detonating explosives as defined in claim 1 wherein the self-explosive solid compound is hexanitromannitol.

4. Plastic detonating explosives as defined in claim 1 wherein the self-explosive solid compound is cyclotrimethylene-trinitramine.

5. Plastic detonating explosives as defined in claim 1 wherein the continuous matrix contains a cellulose ester as a thickening agent.

6. Plastic detonating explosives capable of being stored continuously at low temperatures without setting irreversibly hard which comprise a self-explosive solid compound from the group consisting of self-explosive non-aromatic crystalline solid nitric esters and cyclotrimethylene-trinitramine distributed through a continuous matrix comprising the liquid mixture of nuclear dinitro compounds obtainable by direct dinitration of secondary-butylbenzene.

7. Plastic detonating explosives capable of being stored continuously at low temperatures without setting irreversibly hard which comprise a self-explosive solid compound from the group consisting of self-explosive non-aromatic crystalline solid nitric esters and cyclotrimethylene-trinitramine distributed through a continuous matrix comprising a liquid mixture of dinitro tertiary-butylbenzene and the dinitration product of secondary-butylbenzene, said liquid mixture freezing below —15° C. and containing at least 60% of the dinitration product of secondary-butylbenzene.

8. Plastic detonating explosives capable of being stored continuously at low temperatures without setting irreversibly hard which comprise a self-explosive solid compound from the group consisting of self-explosive non-aromatic crystalline solid nitric esters and cyclotrimethylene-trinitramine distributed through a continuous matrix comprising a liquid mixture of dinitro-cumene and the dinitration product of secondary-butylbenzene, said liquid mixture freezing below —15° C. and containing at least 10% of the dinitration product of secondary-butylbenzene.

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