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CAST EXPLOSIVES COMPRISING CYCLOTRIMETHYLENE TRINITRAMINE AND NITROTOLUENES

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This invention relates to a process for making crack-resistant cast explosives; more particularly it relates to a process for making trinitrotoluene-containing explosives which are highly resistant to cracking under thermal shock. The invention also relates to the products formed by the above process.

Trinitrotoluene (TNT) has been known for many years to possess properties that make it well suited for use in making cast explosives. It is highly stable over long periods of storage, is relatively insensitive to shock or blows, and forms no sensitive explosive compounds by reaction with metals. Furthermore, it melts at a relatively low temperature, so that it is well adapted for forming cast explosive charges, since fusion can be brought about by use of hot water or low pressure steam.

While TNT has the foregoing favorable properties for employment as the explosive for cast charges, it has the serious disadvantage that cast explosives containing it are highly susceptible to cracking under thermal shock. Inasmuch as large changes in temperature are unavoidable in manufacturing and handling of cast explosives, elaborate precautions must be taken in order to obtain sound castings.

It is generally believed that cast explosives crack because of excessive stresses and strains set up in the charge during freezing and subsequent thermal cycling. It is believed that these stresses and strains sometimes exceed the physical strength of the explosive: fracture or cracking is produced. The use of various additives to increase the physical strength of the explosive to the point where it will withstand all normal stresses and strains has been suggested. However, no additive has been found prior to this invention which substantially reduces the cracking of cast explosives and does not prohibitively interfere with such requisite properties as dimensional stability, impact sensitivity, casting properties and others.

It is, therefore, an object of this invention to provide a process for making trinitrotoluene-containing cast explosives which are highly resistant to cracking.

It has been found that the above and other objects are accomplished by the incorporation of proportionately small amounts of a mixture comprising orthonitrotoluene (ONT) and paranitrotoluene (PNT) into a molten mixture of trinitrotoluene-containing explosive, thoroughly mixing the ingredients and casting the melt into the desired shape.

The surprising results obtained by the use of the above mixture are due to the effect of a ternary eutectic mixture formed by the para-, ortho-, and trinitrotoluene. In composition B, an explosive mixture of about 60 percent RDX (cyclotrimethylene trinitramine) and 40 percent TNT, the eutectic formed has a composition of 65.5 percent ONT, 19.5 percent PNT and 15 percent TNT, and has a melting point of −19.5° C. Although the exact mechanism of crack prevention by the eutectic is not known, one possible explanation may be that the low melting eutectic formed with TNT tends preferentially to redissolve the strained crystals since these crystals possess a higher free energy than an unstrained crystal. The dissolved material is then re-deposited in the form of stress free crystals. Further, since the tutectic is acting on the crystals, there is a definite surface lubrication effect that adds to the stress relief.

In order to make a comparative study of the effect on crack resistance of various additives, a severe thermal shock cycle has standardized for use on the cast explosives and an index was formulated for evaluating the results. The following index was used:

$$I=\frac{WL}{(\Delta t)}\frac{1}{2}[f(n)]$$

Where I is the index number, W is a function of the width of the crack, L the length of the crack in centimeters, Δt the range of the temperature cycle and $f(n)$ is a function of the number of cycles. Three classes of cracks were defined as follows: wide open cracks, medium cracks and very fine cracks with assigned width factors of 5, 3 and 1.5 respectively. The cracks showing definite cleavage were selected as the wide open cracks, those appearing as fine lines or checks were generally considered the very fine cracks and those more clearly defined than the fine cracks and not showing any visible fracture or cleavage were selected as the medium cracks. Δt was arbitrarily raised to the one-half power to approximate its effect on cracking. This was necessary because several different thermal cycles were used before all the testing was completed. While the magnitude of the values in this empirical formulation might not be absolute, they give a statisfactory relative evaluation.

Intentionally severe and abrupt thermal shock cycles of 65° C.→0° C.→65° C. for composition B and 65° C.→20° C.→65° C. for Baratol were used and all castings in a particular batch were cycled together. The composition B cycle consisted of heating the charges in a 65° C. industrial type oven for eighteen hours, removing to an agitated ice-water bath for six hours and then reheating in the oven for eighteen hours. They are then removed from the oven, allowed to cool, the cracks measured and the index computed. Thereafter they were sectioned and examined for internal cracking. The Baratol cycle consisted of heating the charges in an oven at 65° C. for eighteen hours, then placing them in a deep freeze unit for 18 hours after which they were again heated in the 65° C. oven for eighteen hours; after the forty-four hour cycle the chanrges were allowed to cool to room temperature before the cracks were evaluated. In general, it was found that internal cracking was proportional to external cracking.

In making the tests to determine the effectiveness of the various additives the castings were made from open kettle melts and the melting procedure and pouring temperature were standardized. A medium sized shaped charge was used and a standard casting procedure was adopted which resulted in a charge free from all stress and feeding cracks. The top contours on all charges were machined to approximately a 9.25 inch radius contour in order to insure charge uniformity and to obtain a smooth top surface for examining the cracks. In order to get a reliable statistical evaluation of the effect of the additives on crack prevention a number of charges were used to test each additive and these were taken from the same melt, cast with a standard cooling procedure and thermally shocked simultaneously.

Following is a tabulation of the results obtained in composition B and Baratol (about 76 percent barium nitrate and 24 percent TNT) using the above procedures and index. The index values are the average of a batch of a number of castings. It will be noted that the average of the values obtained without additives is 25. This value can be used as a standard for comparing the effect of the various additives on crack resistance. All index numbers are rounded off to the nearest whole integer. Amounts are shown as percentages of composition B or Baratol and the ONT–PNT mixture is in the ratio of 1 to 1.

COMPOSITION B

Additive	Amount of Additive	Average I of Batch	Average I
None		31	25
Do		24	
Do		20	
ONT	.4	21	
PNT	.4	18	
ONT–PNT	.4	6	7
ONT–PNT	.4	8	
ONT–PNT Cetyl-Palmitate	.45	18	
ONT–PNT Iso Butylene Glycol	.45	17	
ONT–PNT H-Hexadecane	.45	12	

BARATOL

None		19	18
Do		17	
ONT–PNT	0.6	7	9
ONT–PNT	0.6	10	

The combinations comprising the last three additives in the first table were used to determine the effectiveness of ternary additives. The third additive was one which showed some promise by itself and it was felt that it might contribute something beneficial when added with the ONT and PNT; .05 percent by weight of the third additive was added to the ONT–PNT mixture.

The results graphically demonstrate the effectiveness of the ONT–PNT mixture for composition B and Baratol. It is essential that the ONT and PNT be added in the form of a mixture as the addition of either of these compounds alone does not produce the desired result. The optimum ratio of ONT to PNT in the mixture is about 1 to 1 but may vary slightly either way.

Experience has shown that the most convenient method of handling the additives has been to weigh out separately the amounts of ONT and PNT required and make a stock solution by dissolving the para-nitrotoluene in the ortho-nitrotoluene. The required amount of the mixture for any given size melt can then be measured either volumetrically or gravimetrically.

The additives should be added to the melt about ten to fifteen minutes prior to pouring and at a melt temperature below 90° C. In the case of vacuum melts, the addition can be made after breaking the vacuum on the melt.

Following is a tabulation of results of tests made to determine the optimum amount of ONT–PNT additive for composition B and Baratol. Weights are given as percentages of the weight of composition B or Baratol in the charge as the case may be.

Composition B

Percent additive ONT–PNT	I
0.20–0.20	6
0.20–0.20	7
0.34–0.10	7
0.14–0.04	13
0.03–0.01	21
0.10–0.10	14
0.50–0.15	8
0.21–0.07	12
0.20–0.10	9

Baratol

.12–.12	12
.06–.06	11
.04–.04	10
.03–.03	7
.02–.02	12

It will be noted from the above table that the optimum amount of the ONT–PNT mixture having equal amounts of each ingredient is .4 percent for composition B and .06 percent for Baratol. This amounts to between .75% and 1% of additive based on the weight of TNT in composition B.

The following specific examples are given to illustrate preferred embodiments of the present invention but are in no way intended to limit the scope thereof.

One hundred seventy-five pounds of composition B consisting of about 60 percent RDX and 40 percent TNT were melted in a steam kettle and held at a temperature of 85 to 88° C. To the molten mixture formed 0.7 pounds of a mixture of equal amounts of PNT and ONT were added slowly with moderate stirring. After stirring for 15 minutes the resulting mixture was poured into molds and cast. The same procedure was repeated using 175 pounds of Baratol, and 0.10 pounds of the ONT–PNT mixture. After removal from the mold the charges were machined and subjected to the respective thermal shock cycles described above.

The cast explosives were found to have a crack index of 6 and 7 for the composition B and Baratol products respectively and in general were of higher quality than explosives cast by former processes. The use of ONT–PNT additive was found to have no detrimental effect on such properties of the cast explosive as dimensional stability, impact sensitivity, detonation velocity and rheological characteristics. It was found that the use of the above additive improves the casting properties of both composition B and Baratol in that it permits faster cooling procedures and the casting of certain type charges which formerly could not be successfully cast.

It is thus seen that the process of the invention provides a means of producing cast trinitrotoluene-containing explosives which are highly resistant to cracking and are superior in other characteristics to cast explosives made by prior methods.

While there have been described what are considered to be preferred embodiments of the present invention, it is to be understood that the invention of this application is not limited to the specific examples herein recited but that numerous modifications and variations thereof may be made without departing from the scope of the invention as set forth in the appended claims.

What is claimed is:

1. A process of preparing a cast explosive composition which is resistant to thermal cracking which consists in heating a composition consisting of 60% cyclotrimethylene trinitramine and 40% trinitrotoluene to a molten condition but not in excess of about 90° C., adding thereto a mixture consisting of orthonitrotoluene and paranitrotoluene, said added mixture being in an amount equal to about .75% to 1% of the trinitrotoluene present in the composition, mixing the composition and added mixture, and casting the resulting melt into a desired shape.

2. A process of preparing a cast explosive composition which is resistant to thermal cracking which consists in heating a composition consisting of 60% cyclotrimethylene trinitramine and 40% trinitrotoluene to a molten condition but not in excess of about 90° C., adding thereto a mixture consisting of equal parts of orthonitrotoluene and paranitrotoluene, said added mixture being in an amount equal to about 1% of the trinitrotoluene present in the composition, mixing the composition and added mixture, and casting the resulting melt into a desired shape.

3. A cast explosive composition comprising approximately 60% cyclotrimethylene trinitramine and 40% trinitrotoluene to which has been added a mixture of equal amounts of orthonitrotoluene and paranitrotoluene, said mixture being present in an amount equal to about 1% of the trinitrotoluene in the composition.

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