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## FREE FLOWING CRYSTALLINE ORGANIC DETONATING COMPOUND WITH ORGANIC FLUORINE POLYMERS

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The present invention relates to a novel explosive composition. More particularly, the present invention relates to an improved explosive composition which is free flowing, readily formed into coherent masses, and of high thermal stability.

In general, crystalline organic detonating compounds have found widespread usage in the explosives art in such devices as initiators, detonating fuse, shaped charges, and other explosive specialties. Cyclotrimethylenetrinitramine, more commonly known as RDX, has been of special value in such applications because of its relatively high degree of thermal stability, its melting point being about 390° F. and its "fume-off" point about 550° F. To a lesser extent, HMX (cyclotetramethylene-tetranitramine), which is a relative of RDX and exhibits even greater thermal stability, has been used in the aforementioned applications. More recently, an additional compound of this class, picryl sulfone (melting point, about 630° F. with decomposition) has replaced the specified nitramines in certain explosives applications wherein even the latter compounds are lacking in thermal stability. For example, in copending application Serial No. 774,766, now abandoned, filed by P. Barnhard, B. Chudzik, and D. N. Thatcher and assigned to the present assignee is described a jet-perforating system for use in the so-called "hot" oil wells (wells of extremely high-temperature) and wherein picryl sulfone constitutes the explosive component of the shaped charges and the detonating fuse. This assembly was developed in view of the fact that the conventional RDX-containing assembly lacked sufficient thermal stability for use in these "hot" wells.

Because of their crystalline nature, such compounds as RDX, HMX, and picryl sulfone in most cases must be treated with an additive to impart to them the characteristics required for their handling or processing. When untreated, the discrete particles comprising these materials generally have poor flowing properties which tend to make the particles bridge deleteriously during their introduction into initiator shells or the like. Furthermore, due to the lack of cohesive forces among these discrete particles, the plain, or untreated, RDX, HMX, or picryl sulfone cannot be pressed into pellets or the like, for example those used in shaped charges, of sufficient coherency to maintain their form when removed from the die or when subjected to the usual mechanical stresses incurred in handling.

To provide the necessary free-flowing properties, these crystalline explosives usually are treated with a graining agent, i.e. an additive imparting free flow, which coats and lubricates the larger grains and agglomerates the finer crystals. Numerous graining agents are known, including graphite, wax, gums, shellacs, polyvinyl alcohol, and a variety of plastics and resins. In many instances, these graining agents act also as binders which facilitate the obtaining of the afore-mentioned coherent forms. Such adhesive materials as wax, gums, shellac and the like exhibit this dual function, while graphite does not perform reliably as a binder, acting rather as a die lubricant.

Although for most explosives applications, the selection of the proper additive with which to modify the properties of the crystalline explosive is not difficult because of the wide variety of such materials known to the art, a serious

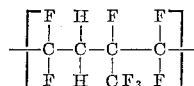
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problem is introduced when the application involves high temperatures, e.g. those exceeding about 325° F., because the conventional graining agents and binders are not suitable for use at such temperatures. For instance, wax, which provides the necessary binding action, migrates out of compressed explosive when the explosive is exposed to the high temperatures, and may desensitize adjacent explosives. Thus, wax cannot be used as a binder for the pressed charge of a perforator for use at high temperatures nor as a graining agent for loose charges exposed to high temperatures. On the other hand, graphite, which is relatively unaffected by high temperatures, cannot be relied upon to give pressed masses of the necessary coherency, although it serves well as a graining agent for loose charges destined for high-temperature applications. Obviously, therefore, although a number of crystalline organic detonating compounds are known which exhibit an acceptable degree of thermal stability, the lack of a versatile additive which imparts the requisite free-flow and coherency to these compounds and at the same time is unaffected by high temperatures constitutes a serious problem in the art.

Accordingly, an object of the present invention is the provision of a thermally stable explosive composition. Another object of the present invention is the provision of such an explosive composition which is of a free-flowing nature and can be pressed to form coherent shaped objects. A further object of the present invention is the provision of a thermally stable, free flowing, satisfactorily pressed explosive composition which can be easily prepared. Other objects will become apparent as the invention is further described.

I have found that the afore-mentioned objects may be achieved when I provide an explosive composition comprising a crystalline organic detonating compound having a melting point of at least 325° F. admixed with a copolymer of vinylidene fluoride and hexafluoropropylene.

The following examples serve to illustrate specific embodiments of the explosive composition of the present invention. However, they will be understood to be illustrative only and not as limiting the invention in any manner. The vinylidene fluoride-hexafluoropropylene copolymer used in the exemplified experiments is "Viton," available commercially in two grades (A and A-HV). This copolymer contains 30 to 70% by weight, preferably 53 to 70%, of vinylidene fluoride. Its recurrent structural unit is:



polymers having molecular weights as high as  $15 \times 10^4$  having been prepared. "Viton" A and A-HV, light-colored, translucent polymers, soluble in low-molecular-weight ketones, exhibit a Mooney viscosity (ML-4/212° F.) of 67 and 180, respectively, both having a specific gravity of about 1.82. Further information on "Viton" is available in the following references: Dixon, S., et al., Ind. Eng. Chem. 49, 1687-90 (1957), Development Products Report No. 3, "Viton" A (April 15, 1957), and Report No. 58-3, "Viton" A and "Viton" A-HV (May 1958).

### Example 1

Two 98-gram samples of picryl sulfone were grained with the vinylidene fluoride-hexafluoropropylene copolymer, one being grained with "Viton" A and the other with "Viton" A-HV, in accordance with the following procedure. A 10% solution of each of the two grades of "Viton" in acetone was prepared. Each solution in the amount of 20 milliliters was mixed with a sample of the picryl sulfone, and the resultant mixture was forced

through a No. 20 silk bolting cloth. The grained mixes, consisting of 98 grams of picryl sulfone, 2 grams of "Viton," and residual acetone, were dried overnight in an 160° F. oven to remove the residual acetone. After drying, the free-flowing grains of each of the two mixes were tested for impact sensitiveness in the conventional drop test (5-kilogram weight), the 50% detonations point being 16 inches and 25 inches for the "Viton" A and "Viton" A-HV mixes, respectively. Lots of the two mixes could be maintained at 400° F. for about 18 hours without deleterious effect, and the grained mix "fumed-off" at 500° F. When the mixes were consolidated into shaped charges for use in jet perforators, ½ % by weight of graphite was added to the mix to act as a die lubricant facilitating removal of the pressed masses from the die. Strong, cohesive charges of picryl sulfone-"Viton" mixture were obtained which gave satisfactory performance in jet perforators of standard design, the penetrations into steel target plates being 3.46 and 3.53 inches, respectively, for the "Viton" A and "Viton" A-HV mixes.

#### Example 2

Picryl sulfone in the amount of 49 parts was mixed with 10 milliliters of a 10% solution of "Viton" A in acetone. The mixture was poured into boiling water and agitated therein until no odor of acetone could be detected, an agitation period of about 10 minutes. The supernatant water then was decanted, and the water-wet granules were dried overnight in a 160° F. oven. To the dried granules was added ½ % by weight of graphite. The mix was pressed into shaped charges for jet perforators of conventional design. When the charges were tested in these perforators, an average penetration of 3.51 inches into steel targets was obtained.

#### Example 3

A number of mixes of picryl sulfone and "Viton" were prepared in accordance with the procedure of Example 1. In these mixes, various quantities of "Viton" A or A-HV were used to give compositions having "Viton" contents of 1-5%. The mixes and the results of the conventional drop test (5-kilogram weight) made thereon are summarized in the following table.

TABLE I

| Mix No. | "Viton" * Content (percent by wt.) | 50% Detonations Point (in.) |
|---------|------------------------------------|-----------------------------|
| 1       | 1                                  | 16                          |
| 2       | 2                                  | 17                          |
| 3       | 3                                  | 25+                         |
| 4       | 4                                  | 19                          |
| 5       | 1                                  | 22                          |
| 6       | 2                                  | 21+                         |
| 7       | 3                                  | 17                          |
| 8       | 4                                  | 19                          |
| 9       | 5                                  | 18+                         |

\*Mixes No. 1-4 contained "Viton" A, whereas Mixes No. 5-9 contained "Viton" A-HV.

As shown by the following examples, an explosive composition of adequate sensitiveness and exhibiting good flowing properties and coherency after pressing can be readily obtained, without sacrifice of thermal stability, by the addition of a vinylidene fluoride-hexafluoropropylene copolymer to a thermally stable crystalline organic detonating compound. Such compounds may be defined as those crystalline high explosives organic in nature which neither melt nor decompose at temperatures less than 325° F. Among these materials would be included the previously discussed RDX, HMX, and picryl sulfone. In view of its very high temperature stability, picryl sulfone is especially suited for high-temperature applications, and, thus, its use as the detonating constituent of the instant composition constitutes a preferred embodiment of the present invention.

The vinylidene fluoride-hexafluoropropylene copolymers, which are sold under the registered trademark "Viton," are synthetic elastomers exhibiting exceptional heat stability. In fact, these elastomers can be cured by application of heat alone. Therefore, although the curing of the elastomer component of the composition is not necessary, the exposure of the composition, for example in the form of coherent shaped masses to high temperatures may be considered beneficial in that the resultant curing process imparts greater strength to the mass. Preferably, the elastomer component is added to the explosive in the amount of 1 to 5% by weight. When lesser amounts are used, the composition is somewhat lacking in cohesiveness. Although somewhat greater amounts may be incorporated without deleterious effect, for example on sensitiveness, increases in elastomer content may result in a slight stickiness, which interferes in loading operations. Furthermore, in view of the fact that completely satisfactory results are obtained when the composition contains no more than 5% of the elastomer, use of greater amounts of this comparatively high cost ingredient is impractical on an economic basis.

As has been exemplified, other additives may also be employed in the composition so long as they exhibit the requisite degree of thermal stability. For example, it may be desirable to include a slight amount of a thermally stable lubricant, e.g., graphite, in the composition when it is to be pressed inasmuch as the lubricant facilitates removal of the pressed masses from the die.

As illustrated, the explosive composition of the present invention may be readily prepared in a simple and safe manner. The exact method used to prepare the explosive composition is not critical, since a number of conventional procedures can be adapted or alternate procedures may be readily devised. The composition may be prepared without difficulty in accordance with a conventional graining technique. That is, a solution of the elastomer in a suitable solvent such as acetone is thoroughly admixed with the detonating compound, and the elastomer-explosive mixture is forced through a bolting cloth. Removal of residual solvent from the grains by evaporation provides free-flowing grains suitable for pressing alone or mixed with the lubricant, which may be added to the dried grains. On the other hand, since the afore-described graining technique is a hand operation which must be effected on a relatively small scale, it may be advantageous to employ the mixing technique described in Example 2. In this latter method, the acetone-containing mixture is not grained through the bolting cloth but rather is agitated in boiling water, which drives off the acetone to give water-wet granules, which are thereafter dried. These dry free-flowing grains are also readily pressed. Alternative to either of these procedures is one involving the spraying of the elastomer solution on to the explosive particles while they are being tumbled.

The invention has been described in detail in the foregoing. However, it will be apparent to those skilled in the art that many variations are possible without departure from the scope of the invention. I intend, therefore, to be limited only by the following claims.

#### I claim:

1. A free-flowing, readily pressed explosive composition of high thermal stability which consists essentially of a crystalline organic detonating compound having a melting point of at least 325° F. selected from the group consisting of picryl sulfone, cyclotrimethylenetrinitramine and cyclotetramethylenetetranitramine admixed with a copolymer of vinylidene fluoride and hexafluoropropylene in an amount between 1 and 5% by weight of the composition.

2. An explosive composition according to claim 1, wherein said detonating compound is picryl sulfone.

3. An explosive composition according to claim 1, wherein said copolymer contains 30 to 70% by weight of vinylidene fluoride.

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4. An explosive composition according to claim 1, wherein 0.5% by weight of graphite is present as a lubricant.

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