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Texas Tech University, and The University of Texas System

## Literature Review of the Lifetime of DOE Materials: Aging of Plastic Bonded Explosives and the Explosives and Polymers Contained Therein

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AMARILLO NATIONAL RESOURCE CENTER FOR PLUTONIUM/  
A HIGHER EDUCATION CONSORTIUM

A Report on

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Explosives and the Explosives and Polymers Contained Therein**

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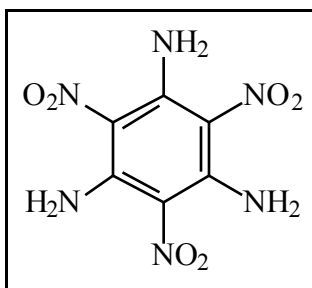
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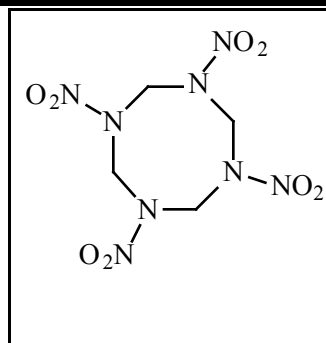
## *Abstract*

There are concerns about the lifetime of the nation's stockpile of high explosives (HEs) and their components. The DOE's Core Surveillance and Enhanced Surveillance programs specifically target degradation of HE, binders, and plastic-bonded explosives (PBXs) for determination of component lifetimes and handling procedures. The principal goal of this project is to identify the decomposition mechanisms of HEs, plasticizers, and plastic polymer binders resulting from exposure to ionizing radiation, heat, and humidity. The primary HEs of concern are 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) and 1,3,5,7-tetranitro-1,3,5,7-tetraazocyclooctane (HMX). Hexahydro-1,3,5-triazine (RDX) is closely related to these two compounds and is also included in the literature review. Both Kel-F 800 and Estane are polymers of interest. A stabilizer, Irganox 1010 (Ciba Specialty Chemicals Corp. USA), and an energetic plasticizer that is a blend of acetaldehyde 2,2-dinitropropyl acetal and formaldehyde 2,2-dinitropropyl acetal (also known as bis(dinitropropyl) acetal and bis(dinitropropyl) formal, respectively), are also of interest, but the focus of this report will be on the explosives and polymers.

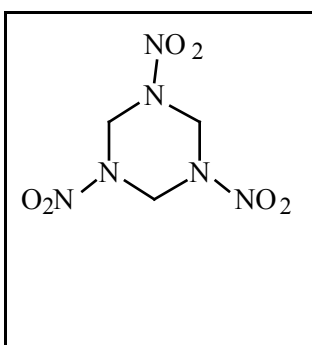
The following is a literature review that provides background on the synthesis, degradation, and techniques to analyze TATB, HMX, RDX, Kel-F 800, Estane, and the PBXs of these compounds. Figure 1 contains the chemical structures of each of these compounds. As there are many factors that can influence degradation of materials, the degradation discussion will be divided into sections based on each factor and how it might affect the degradation mechanism. The factors reviewed that influence the degradation of these materials are exposure to heat, UV- and -irradiation, and the chemistry of these compounds. The following is a recently compiled accounting of the available literature.



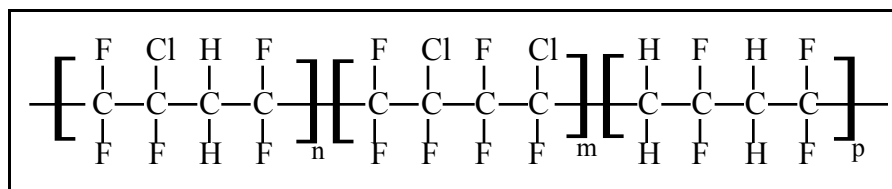
(a) 1,3,5-triamino-2,4,6-trinitrobenzene (TATB)



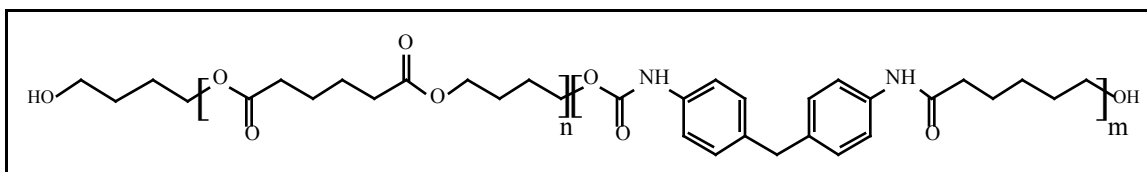
(b) 1,3,5,7-tetranitro-1,3,5,7-tetraazocyclooctane (HMX)



(c) Hexahydro-1,3,5-triazine (RDX)



(d) Kel-F 800



(e) Estane 5703-F1

**Figure 1:** Chemical Structures of Compounds of Interest

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# 1. SYNTHESIS

## 1.1 EXPLOSIVES

Most of the explosives materials in this project will be provided by Pantex. However, in order to properly analyze some of the degradation products, some compounds very similar to the original explosive will need to be synthesized. Literature has also been included regarding the synthesis of the original compounds.

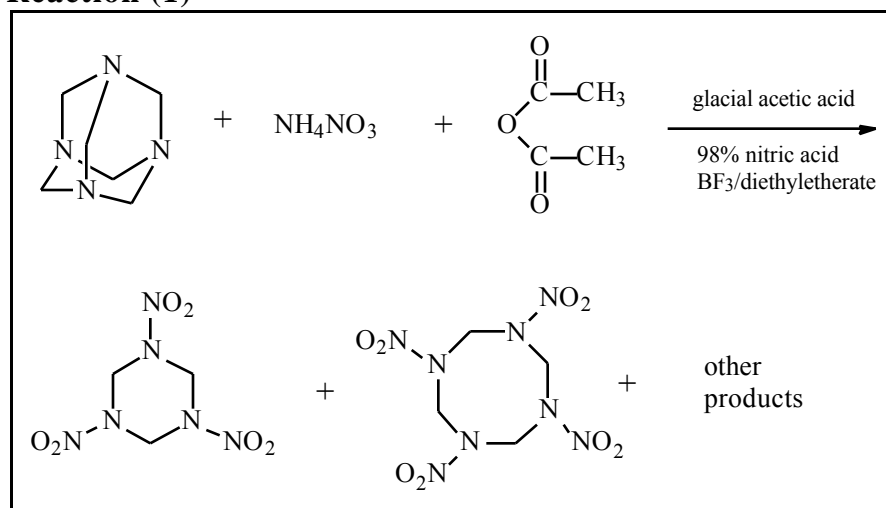
RDX and HMX were some of the earlier explosives developed. They are not as shock sensitive as TNT and other more well known explosives, but are still fairly easy to detonate. In their synthesis of RDX at 46°C, Singh, et al. (1973) used hexamine (in glacial acetic acid), ammonium nitrate (98% nitric acid), and acetic anhydride with boron trifluoride diethyletherate catalyst in acetic acid and acetic anhydride. Reaction (1) is the chemical reaction to form the RDX and HMX products. The main product of this reaction is RDX with some HMX and other by-products. Addition of nitric acid pushed the reaction to completion. Methyl ethyl ketone was used as a solvent to extract the HMX and RDX. Abel et al. (1981) provided a bibliography of several articles which included the synthesis of RDX and HMX. Government reports and ACS publications also describe synthetic routes to form RDX and HMX (Coon, 1974 and Gilbert, 1976).

The development of TATB grew from a need of an explosive less sensitive than RDX

and HMX (Urbanksy et al., 1978; Dobratz 1995). There are several publications discussing the synthesis and reactions of TATB. Dobratz (1995) describes the history of the synthesis and characterization of TATB and TATB in PBXs (Dobratz, 1995). An interesting side note is that in early syntheses, TATB was not considered to be an explosive. TATB was first synthesized in 1887-1888 by mixing 1,3,5-tribromo-2,4,6-trinitrobenzene (TBTNB) with cold alcoholic ammonia and refluxing for about 30 minutes, with more alcoholic ammonia added as needed (Dobratz, 1995; Jackson, et al. 1888). TATB was prepared later by refluxing pentanitroaniline with aqueous ammonia (Dobratz 1995; Flürscheim, et al. 1929). In 1937, TATB was produced in 80% yield by reacting 2,4,6-trichloro-1,3,5-trinitrobenzene (TCTNB) with ammonia (Dobratz, 1995; Backer, 1937). In the late 50's and early 60's, TATB was known to be an insensitive explosive and was prepared according to the procedures just discussed (Dobratz, 1995; Hill & Taylor, 1960; Kaplan and Taylor, 1961). TCTNB became the preferred starting material shortly thereafter (Dobratz, 1995; Hill & Taylor, 1960; Kaplan and Taylor, 1961).

Government research at Sandia National Laboratory (O'Keefe and Gurule, 1978) and Pantex (Estes, 1977; 1979) was done to make small modifications in the synthesis of TATB in order to remove impurities or to change the particle size.

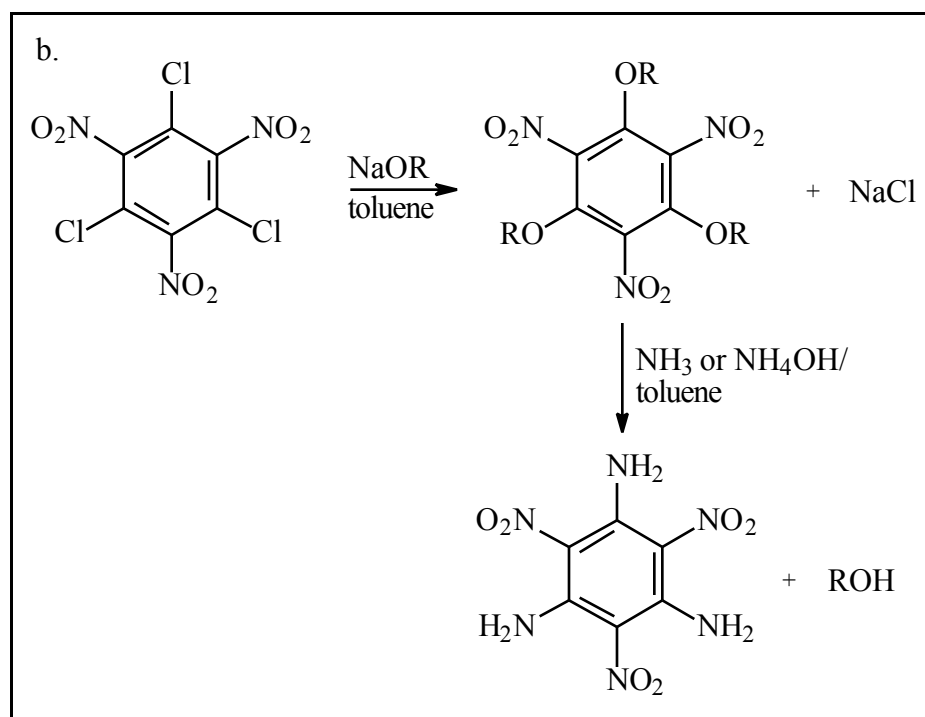
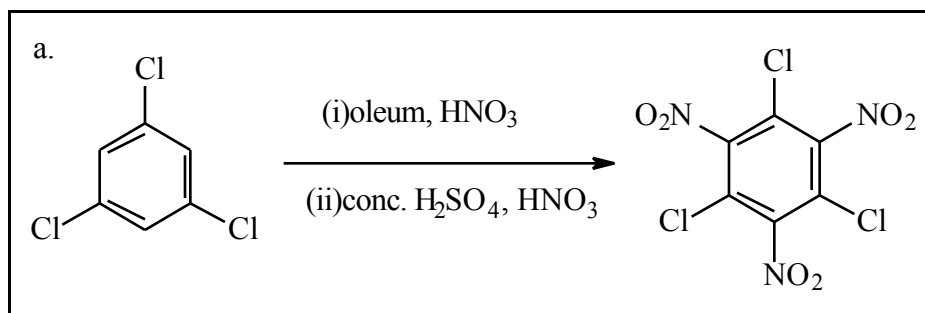
### Reaction (1)



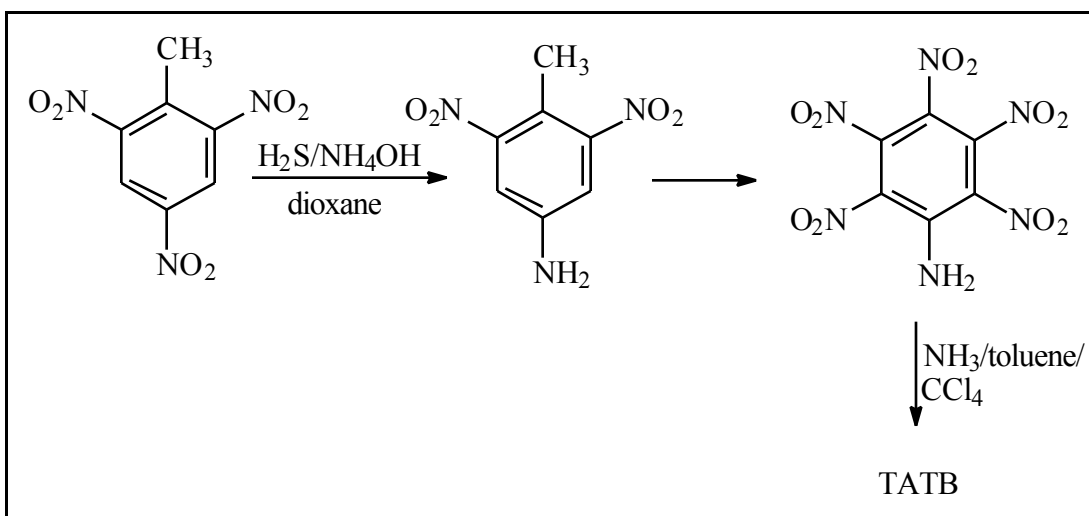
O'Keefe and Gurule (1978) dealt with an improved method of synthesis of TCTNB (2a) and an extensive literature review of the development of TCTNB synthesis. Another synthesis of TATB proceeds using 1,3,5-trichloro-2,4,6-trinitrobenzene as seen in reaction (2b). The Pantex researchers investigated methods to reduce chlorine contamination of the sample and found their best synthetic route to be reaction (2b). Urbansky and Vasudeva (1978) presented a similar synthetic route to TATB, but started with aniline to form 1,3,5-trichlorobenzene, the precursor used by O'Keefe to form TCTNB and then TATB. Another method

showed the reaction of hexanitrobenzene with excess  $\text{NH}_3$  to produce a 95% yield of TATB (Nielson et al., 1979). As shown in (3), Atkins et al. (1986) started with trinitrotoluene (TNT), a rather sensitive explosive, to form 2,3,4,5,6-pentanitroaniline using  $\text{H}_2\text{S}$  and  $\text{NH}_4\text{OH}$ , then formed TATB after adding  $\text{NH}_3$ , toluene, and  $\text{CCl}_4$ . Ott and Benzinger (1991) synthesized TATB by ammonolysis of 3,5-dichloro-2,4,6-trinitroanisole in toluene at room temperature (see Reaction 4). The TATB produced was >95% yield and of relatively high purity (~0.8% chloride), but the particle size was smaller than desired.

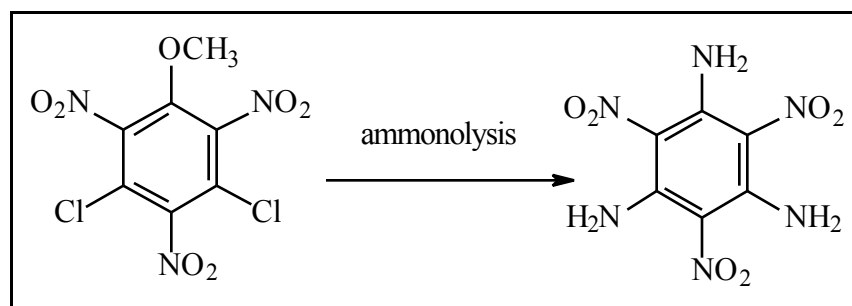
### Reaction (2)



### Reaction (3)



### Reaction (4)



One of the difficulties in studying TATB is its incredibly low solubility. However, Rogers (1986) reacted TATB with  $\text{NH}_3$  in methanol to form hexaaminobenzene, followed by the formation of 1,4,5,8,9,12-hexaazatriphenylene. Harris (1985) found that the reaction of base with TATB to form salts was a relatively simple method of identifying TATB from the by-products, as the TATB salt was a distinct orange versus the red color of the other component salts. TATB has also been mixed with  $\text{H}_2\text{SO}_4$  for  $^{13}\text{C}$  nuclear magnetic resonance (NMR) studies. The acid, however, does perturb the structure of the TATB, so only limited structural information can be obtained from the NMR spectra (Harris, 1979). Structural analysis of TATB will be discussed in more detail in the analytical section.

## 1.2 POLYMERS

Polymers are typically combined with the explosives to form PBXs. The polymers are commercially obtained, so the synthetic routes are proprietary, protected by patents, and limited synthesis literature was available. The polymers that are used have special properties in that they are copolymers containing rigid and flexible sections. It is known that Estane is a copolymer of 1,4-butandiol, 4,4'-phenylmethane diisocyanate, and a macrodiol made from adipic acid and 1,4-butandiol (Lightfoot, et al., 1998). The building blocks of Estane are shown in Figure 2, but the exact synthesis and amounts of n and m are proprietary.

Kel-F 800 is a copolymer of chlorotrifluoroethylene (CTFE) and vinylidene fluoride (VDF) from 3M. The exact synthesis

is not available as it is proprietary information, but in general, fluoroelastomers are made using free radical initiation in an aqueous emulsion under high pressure in order to polymerize the monomers (Overturf, 1997). The initiators are organic or inorganic peroxy compounds, and the emulsifiers are usually a fluorinated acid soap. The molecular weight can be controlled by the ratio of initiator to monomer. Figure 3 shows the two starting monomers and the copolymer. Information on characterization of the polymers will be discussed in more detail in the analytical section.

### 1.3 PLASTIC BONDED EXPLOSIVES

Polymers are combined with explosives in order to minimize their shock sensitivity and therefore make them less dangerous to handle. Hallem (1976) and Kolb and Pruneda (1979) discussed various formulations of TATB with Kel-F 800 and found that different polymers did not change the character of the TATB surface energies. Pruneda et al. (1980) discussed the combination of TATB with Kel-F 800 using various solvents in order to increase the binding of TATB with the polymer. The solvents tried were THF, carbon tetrachloride, and chloroform.

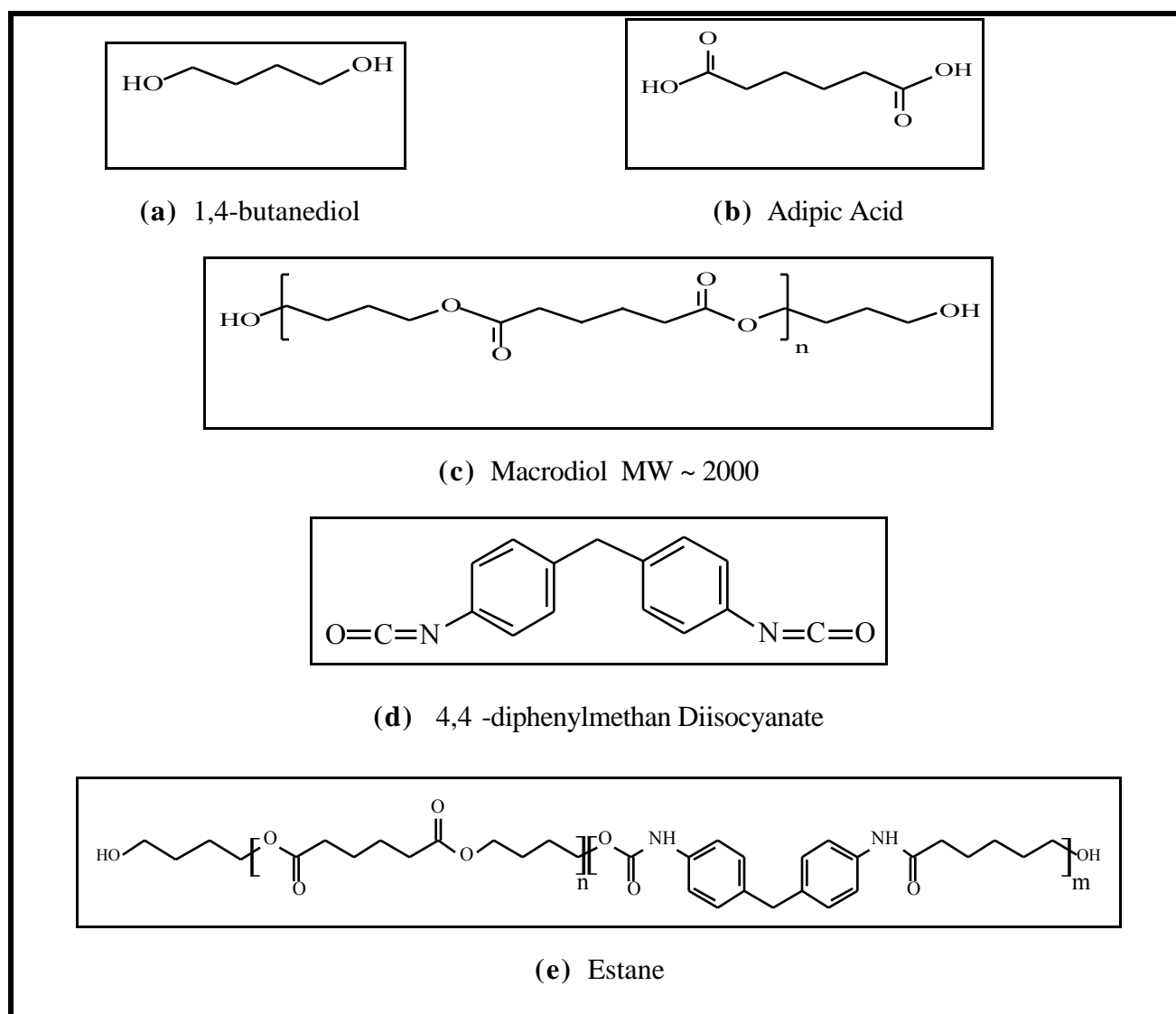
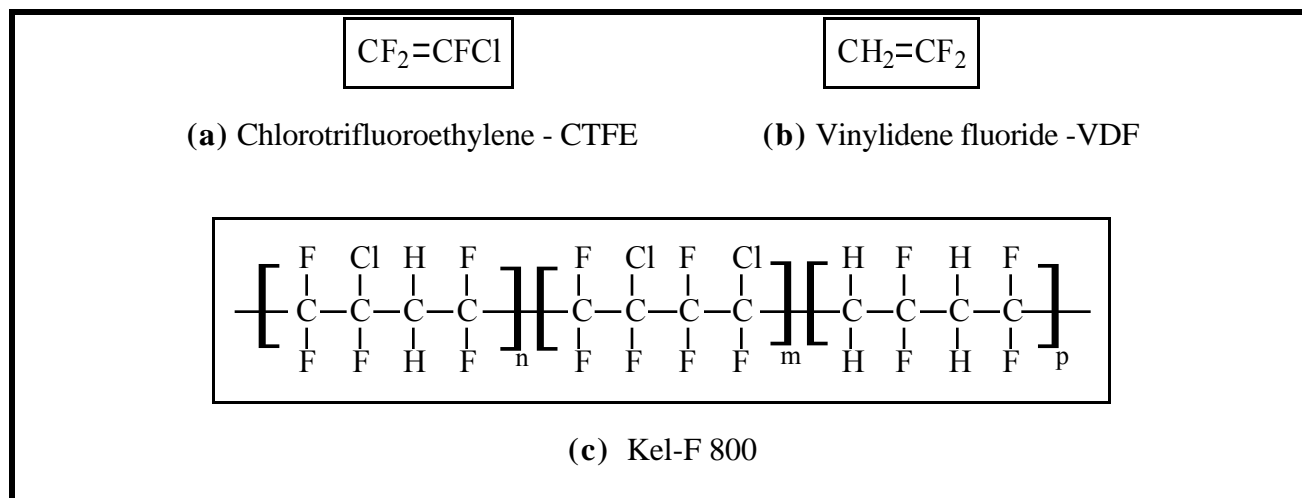
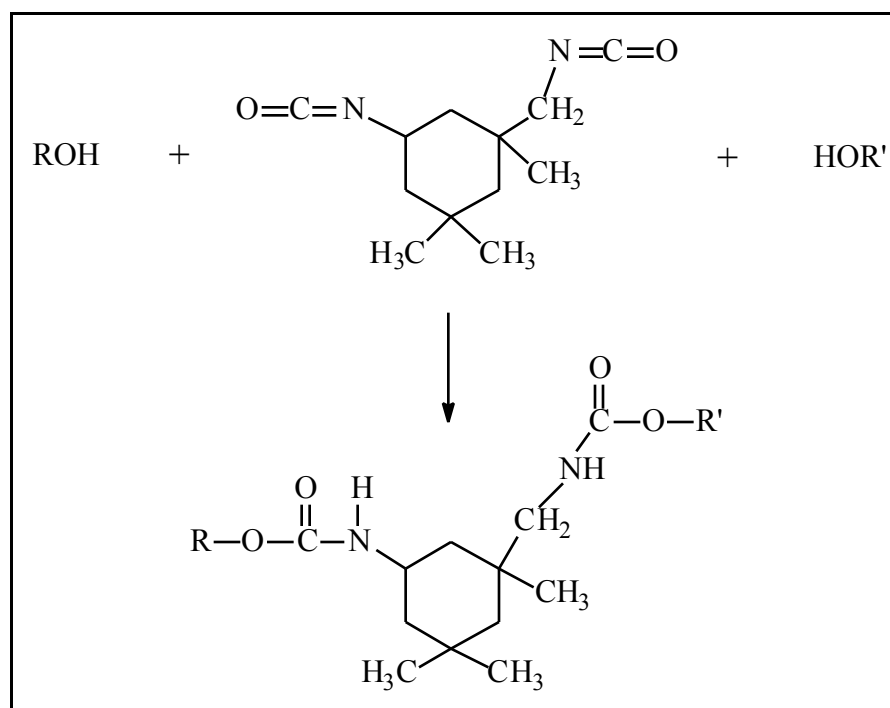


Figure 2: The Building Blocks of Estane



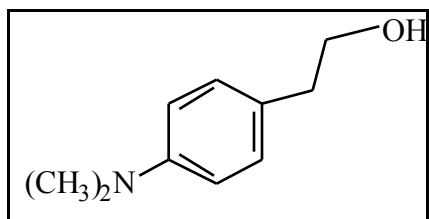
**Figure 3:** The Building Blocks of Kel-F 800

**Reaction (5)**



A more recent British publication presented methods to improve the binding of TATB to hydroxy-terminated polybutadiene (HTPB), the UK choice of binder (Bailey, et al., 1992). The HTPB blocks are reacted with isophorone diisocyanate (IPDI) to form urethane bridging linkages (Reaction 5). The compound 4-(dimethylamino)phenethyl alcohol is an example of one of the chosen binding agents

(see Figure 4). They used two techniques in order to determine the acidity/basicity of TATB, inverse gas chromatography (GC) and dye adsorption using methylene blue and crystal violet. PBXs also contain small amounts of other compounds in order to stabilize the components as well as maintain the flexibility of the polymer. The stabilizer of interest is the hindered phenol Irganox 1010



4-(dimethylamino)phenethyl alcohol

**Figure 4:** Binding Agent for HTPB and TATB

(Ciba Specialty Chemicals Corp. USA)  
(Figure 5a). Irganox 1010 scavenges radicals to form the hindered quinone, also shown in Figure 5a. The energetic plasticizer of interest is a blend of acetaldehyde 2,2-dinitropropyl acetal. and formaldehyde 2,2-dinitropropyl acetal. (see Figure 5b). At this time, these two compounds will not be reviewed, but will be at a later date.

## 2. DEGRADATION

### 2.1 THERMAL

When the HE or polymer is exposed to heat over extended periods of time, how is the material affected? When aging thermally, one looks specifically at heat-generated effects, without the effect of light or other chemicals. However, if an impurity from processing is present, its influence cannot be excluded. In general, when a compound does decompose thermally, free radicals may be generated. In order for decomposition to occur, the temperature must be high enough to cause a particular bond to break. The C-O and C-H bonds tend to be the weakest in aliphatic compounds. Since explosives and polymers are very different materials, they may behave differently. They can also react differently when combined together as PBXs. Each type of material is discussed in the following sections.

#### 2.1.1 Explosives

The degradation of explosives may be tested both for the pure compound and for their PBXs. This section concentrates on the literature associated on the degradation of the explosives without being associated with any other materials. Initial interest was generated in TATB because of its insensitivity, heat resistance, and stability compared to RDX and HMX (Urbanski, et al., 1978; Oxley, et al., 1995). None of the literature examined so far discusses the thermal degradation of HMX and RDX alone, although there is literature dealing with the decomposition of these materials as part of a PBX. TATB sublimates/decomposes before its melting point is reached, at about 250°C (Urbanski, et al., 1978; Oxley, et al., 1995; Sharma et al., 1982; Farber and Srivastava, 1981). Below 200°C, it is reported to be extremely stable and no decomposition is noticed over short time spans (Urbanski, et al., 1978; Oxley, et al., 1995; Sharma et al., 1982; Farber and Srivastava, 1981).

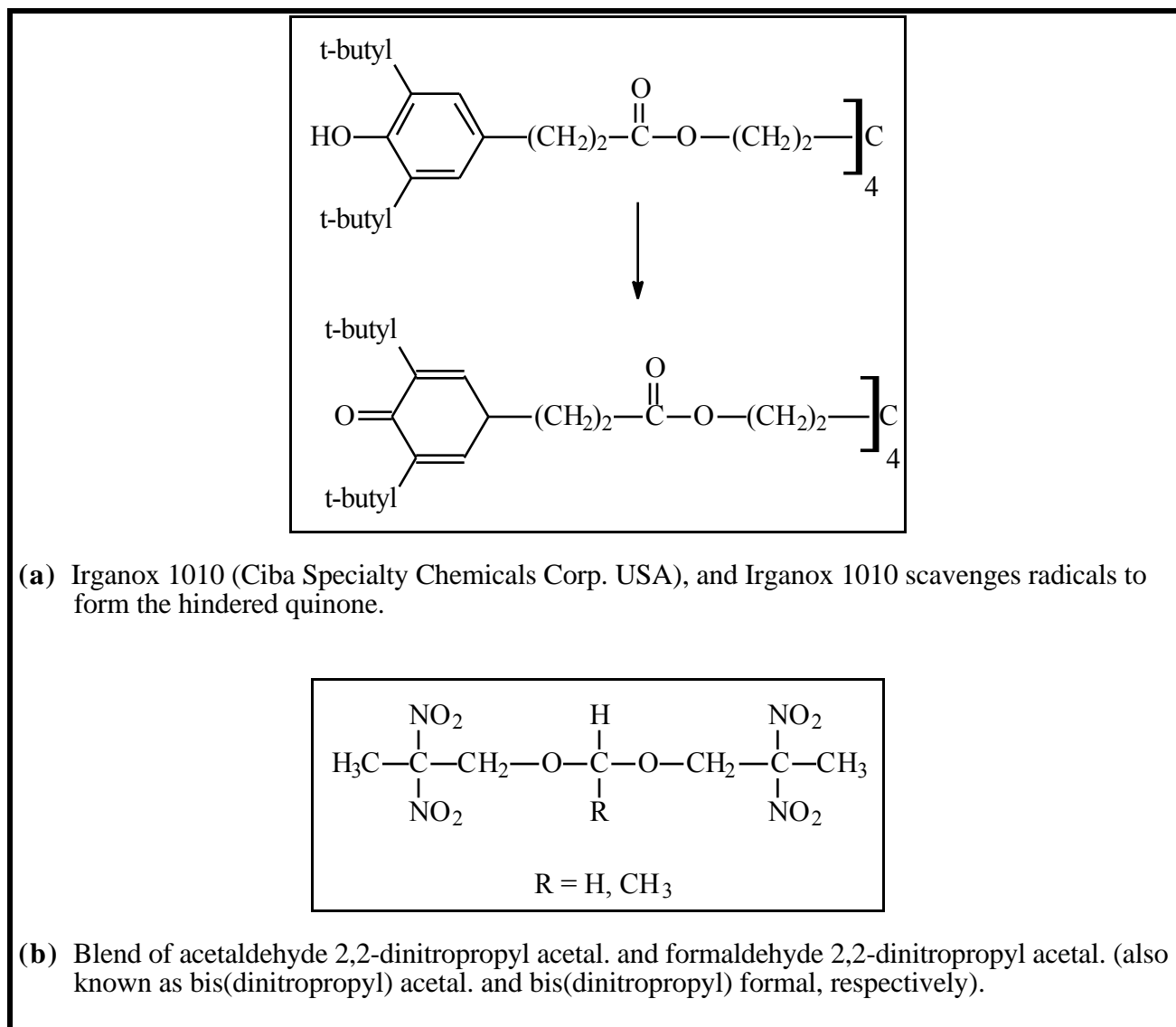
#### 2.1.2 Polymers

As with the explosives, most of the literature discussing the degradation of the polymers in the PBXs focuses on the polymer within a PBX and not on the polymer alone. Yet, without some understanding of the potential mechanisms of degradation of the

polymer alone, elucidation of the mechanism within the PBX becomes more difficult. Of the many different polymers used in HEs, this review focuses on two quite different polymers, Estane and Kel-F. Each will be discussed separately.

Matuszak and Taylor (1981) used a special technique, the flowing after-glow (FLAG) method to monitor the loss of CO<sub>2</sub> from Estane while the polymer was heated. They monitored the Estane over the temperature range of 35 to 234°C. The data indicated that there were three temperature ranges with distinct rate differences, from 75 to 110°C, 127 to 183°C, and 183 to 234°C. The data suggest that the controlling mechanism at lower temperatures is different from that at the higher temperatures, but the authors do not go further than to show the different rate constants in each temperature range. Ferrito (1996) discussed how polyesters degrade at 60°C with a relative humidity of 100%. Polyesters undergo hydrolysis, typically at the ester linkages (R-CO-OR) (Gardner and Martin, 1980). These workers found that if the polyester resin was not completely dry, the polymer would degrade during the molding process. Recent work by Lightfoot and Russell (1998) indicated that the Estane used in PBXs does thermally degrade over time spans of ~3 to 4 months, but the workers suggested the mechanism depends on the water absorption by the polymer and heat application. More discussion follows in the section relating to the chemical degradation of Estane.

Kel-F behaves differently from Estane for several reasons, including its decreased flexibility (Overturf and LeMay, 1997) and increased crystallinity and stability (Reich and Stivala, 1971). Kel-F did not need to have the flexibility of Estane because it was to be used with more insensitive explosives, such as TATB. Upon heating at lower temperatures (<150°C), Kel-F does not break apart into smaller molecules, but rather becomes more crystalline. Increased crystallinity may cause the material to become more brittle and possibly develop cracks, which can substantially alter the mechanical properties of the polymer (Lightfoot and Russell, 1998; Overturf and LeMay, 1997; Hoffman and Caley, 1981). At higher temperatures, Degteva showed that the mechanism of



**Figure 5:** Stabilizers and Plasticizers Found in PBXs

decomposition varied, even from 200-300°C versus that for >300°C (Overturf and LeMay, 1997; Degteva, et al., 1963). At 270°C under vacuum, the data suggested that decomposition of the polymer was initiated by radicals formed from the oxygen dissolved in the polymer. The decomposition eventually led to the formation of HCl and HF. Degteva, et al. (1963) used electron spin resonance (ESR) to determine the remaining polymer to be a polyene. At 300°C under vacuum, HCl is produced preferentially due to the low activation energy of HCl. Using infrared (IR) to monitor the degradation of Aclar (96 % CTFE-co-4 % VDF) at 310-315°C under

vacuum, Sibilja and Paterson (1965) found the major gaseous degradation products were CF<sub>2</sub>=CFCl and CF<sub>2</sub>=CCl<sub>2</sub>, along with CO, CO<sub>2</sub>, and SiF<sub>4</sub> (from reaction of HF with glass). When decomposed in the presence of an oxygen atmosphere, the major product was SiF<sub>4</sub>, with small amounts of CO and CO<sub>2</sub> formed. Sibilja and Paterson (1965) proposed a mechanism for decomposition, as reported in Overturf's unpublished review on Kel-F (Overturf and LeMay, 1997).

### 2.1.3 Plastic Bonded Explosives

Some work on the aging of explosives considered the aging of PBXs, to see if the properties of PBXs change dramatically (Wewerka, et al., 1976; Myers, 1977 & 1979; Breithaupt, 1978; Skidmore, et al., 1998). Most of the work discussed in the literature focuses on changes in the materials and explosion characteristics in order to obtain the lifetime of the PBXs.

Dobratz (1995) discussed early aging tests by Loughran, Wewerka, Cady, and Rogers of Los Alamos National Laboratory. The researchers looked at the aging of TATB and X-0219 (45 wt% TATB, 45 wt% HMX, and 10 wt% Kel-F) at 175 and 204°C for up to 8 weeks and found weight loss significant enough to deem these materials unsuitable for military (Plowshare) applications. Later, lower temperature experiments were conducted. Wewerka, et al. (1976) heated PBX-9501 (94.9 wt% HMX, 5.0 wt% Estane 5703-F1, and 0.1 wt% plasticizer) in sealed ampoules for extended periods of time at 60°C or 75°C, periodically analyzing the headspace gas to determine the storage effects on the explosive's properties. The samples stored in air at 60°C after 64 weeks indicated gas evolution consisting of N<sub>2</sub>, N<sub>2</sub>O, and CO<sub>2</sub>. Gel permeation chromatography of PBX-9501 revealed that Estane 5703-F1 decomposed during storage. The decomposition of Estane led to decreased mechanical strength. Wewerka suggested the decomposition of Estane resulted from oxidative attack of the nitrogen oxides in the explosive. At about the same time, Pritchard (1976) conducted compatibility tests of TATB with Estane 5702-F1, Kel-F 800, and Viton A (in experimental blends, RX-03-AY, RX-03-AX, and RX-03-AZ, respectively). It was found that RX-03-AY, a PBX with Estane, was not suitable for long-term storage.

Coupon tests were done on PBX-9502 and X-0290, both of which consisted of TATB explosive (95 wt %) and Kel-F (5 wt %) (Myers, 1977 & 1979). The coupons were made up of thin disks of the PBX stored under compression in dry air with samples held at 23, 50, 70, and 100°C for up to 2 years. The only significant changes observed in the coupons occurred at 100°C. The author noted that oxygen was consumed; the material stress

and strain increased and rust formed in the stainless steel 304 containers.

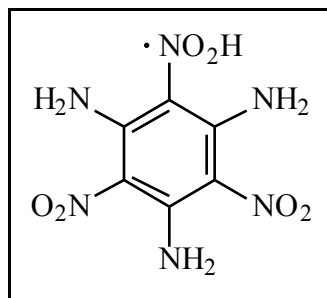
Breithaupt (1978) tested thermal aging of RX-03-BB (92.5 wt % TATB, 7.5 wt % Kel-F 800) by storing samples at 40, 60, 80 and 100°C for 2-32 months and comparing samples thermally aged by cycling the temperature from -55°C for 24 h to 92°C for 24 h. Thermal cycling caused the greatest reduction in mechanical strength, and isothermal aging caused a slight loss in mechanical strength. They suggested any changes in the crystallinity of Kel-F 800 and TATB could cause the changes in the sample mechanical properties, but did not propose an exact mechanism.

Hoffman and Caley (1981) tested the thermal aging of LX-10-1 (94.5 % HMX, 5.5 % Viton A) and PBX-9502 (95 % TATB and 5 % Kel-F 800) at 23, 60, and 74°C for three years. They monitored the dynamic mechanical measurements and molecular weight of the polymers in the PBXs to see if the polymers were degrading, specifically to determine the PBX's life. They found that although LX-10-1 was degrading at a very slow rate, the life of LX-10-1 would exceed 60 years based on the kinetic calculations determined from molecular weight changes. The only changes that could be found in PBX-9502 was in its mechanical properties (shear storage modulus, shear loss modulus, tangent delta, slight change in T<sub>g</sub>) which was attributed to crystallization of the Kel-F 800 binder. However, the changes did not affect the performance of the PBX. Subsequent work by Hoffman, et al. (1989) on the Kel-F 800 binder determined different methods of annealing and molding to reduce the crystallinity changes. More recent work indicates that PBX-9502 is "aging gracefully" and is a very stable PBX (Skidmore, et al., 1998). The researchers compared aged material to unaged material by looking at compressive strength, thermal ignition, and handling sensitivity. They found that any problems that occurred in aged material could be traced to the condition of the original material (Skidmore, et al., 1998).

## 2.2 UV RADIATION

### 2.2.1 Explosives

The explosive of most concern for exposure to ultraviolet (UV) radiation was TATB due to the dramatic color change from yellow to various shades of green when exposed to UV radiation. Several methods were used to examine TATB before and after exposure to this radiation to determine the chemistry behind the color change. Britt, et al. (1981) used ESR to study TATB. The authors studied original solid TATB and dimethylsulfoxide fractions of the UV-irradiated TATB (with solvent removed before ESR analysis). They noted some radical formation in the original TATB due to exposure to ambient light. The radical generated in TATB appeared to be stable for 2 years in air at ambient temperatures. The structure of the radical proposed by this work is shown in Figure 6. Sharma, et al. (1982 & 1979) examined UV and thermal degradation of TATB using X-ray photoelectron spectroscopy (XPS). This work suggested that exposure to UV light resulted in the loss of a  $\text{NO}_2$  group from the ring. Firsich and Guse (1984) disputed the findings of Britt, et al. (1981) after obtaining the original ESR data, recalculating their work, and comparing a theoretical ESR of the proposed radical to the experimental ESR. The ESR spectrum for the actual radical did not match the theoretical ESR data for the proposed radical, but none of the spectra were shown in the publication. Firsich also obtained UV-visible, IR, and Raman spectra to see if they could elucidate the identity of another radical, but came to no specific conclusions (1984). The authors



**Figure 6:** Radical Proposed by Britt et al. (1981)

used electron spectroscopy for chemical analysis (ESCA) on samples of TATB before and after irradiation with a solar simulator lamp and found only a slight loss of  $\text{NO}_2$  signal, a contradiction to the results obtained by Sharma, et al. (1982 & 1979). Firsich (1984) proposed that solar radiation was not as strong as the UV radiation used by Sharma, and therefore proposed that UV light could potentially cause loss of  $\text{NO}_2$ . Comparable studies have been done when irradiating with  $\gamma$ -rays and are discussed in another section.

RDX has also been UV-irradiated and examined by ESR (Pace and Moniz, 1982). Previous ESR work indicated UV- and  $\gamma$ -irradiated samples contained  $\bullet\text{NO}_2$  radicals (Stals et al., 1971). The study by Pace and Moniz (1982) was done on single crystals. The  $\bullet\text{NO}_2$  radical formation is attributed to N-N bond breakage as a result of UV radiation which supported the earlier work, and they go on to discuss specifics in the structure of RDX.

### 2.2.2 Polymers

In general, polymers undergo degradation in the presence UV light because they possess chromophoric groups that absorb energy in this region of the spectrum (Reich and Stivala, 1971; Schnabel, 1981). Light absorption in a polymer consists of a specific interaction of a certain chromophoric group with a photon of given energy. Polymers are capable of absorbing UV radiation, but impurities also participate by absorbing light and initiating reactions once free radicals or activated complexes are formed. Species able to absorb light at wavelengths less than 200 nm to 300 nm are C-C, C-H, O-H, C=O and C=C. Reactions 6 (a), (b), and (c) are examples of how light can generate free radicals that can initiate the degradation of a polymer. Once a reactive species is formed, the polymer can cross link, unzip, or if oxygen is present, react with it much in the same way a radical is formed from thermal degradation. One way to inhibit the degradation is the addition of stabilizers to keep the radicals from reacting further. At this time, no specific publications have been noted on UV degradation for Kel-F 800 or Estane used in PBXs.

### 2.2.3 *Plastic Bonded Explosives*

At this time, no publications relating to UV degradation of PBXs (i.e., the explosive and polymer combined) have been noted.

## 2.3 -IRRADIATION

### 2.3.1 *Explosives*

Dobratz (1995) described the  $\gamma$ -irradiation of TATB by Loughran and Wewerka at Los Alamos in 1973. They used  $^{60}\text{Co}$  as the source with a range of exposure of 0.26 to 21 Mrad. The samples were then aged in 200 torr in air at 175°C from 2 to 16 weeks. They noted that the onset of thermal decomposition started at a lower temperature, and the rate of decomposition increased as the irradiation dose increased. They also monitored the use of free radical inhibitors (quinone, anthraquinone, 1-butene, and NO) under the same conditions but found that these materials did not quench free radical formation.

More recent work indicates that  $\gamma$ -irradiation has a minimal effect on TATB (Skidmore, et al., 1998). The TATB was irradiated in estimated doses of 9 to 70 Mrad, doses comparable to thousands of years of stockpile life. Several different analyses were employed in order to determine if any decomposition of TATB was occurring, including thin layer chromatography (TLC), ESR, IR, mass spectrometry (MS), and differential thermal analysis (DTA)/differential scanning calorimetry (DSC). Other analyses were done to determine any changes in mechanical and explosive characteristics, such as the drop weight impact (DWI) test and the ballistic impact chamber (BIC) test. All the irradiated samples showed some degree of color change to green, and the intensity of the green color was directly related to the irradiation dose. TLC identified mono and difurazan decomposition products only in the 17 and 70 Mrad samples. IR, MS, and scanning electron microscope (SEM) analyses showed no changes in any of the irradiated samples. The ESR spectra from  $\gamma$ -irradiated TATB showed large concentrations of free radicals as well as qualitative spectral differences. The spectra appeared broader than that of room-light-irradiated TATB. However, the tests for explosive characteristics indicated little effect on TATB.

RDX was also monitored after being exposed to  $\gamma$ -irradiation (Stals, et al., 1971). The main result was similar to that seen from exposure to UV radiation, with an increase in free radical content as monitored by ESR.

### 2.3.2 *Polymers*

Absorption of  $\gamma$ -radiation in a polymer is different from UV radiation, for the radiation is a higher energy and it is absorbed non-specifically (Reich and Stivala, 1971; Schnabel, 1981). The radiation interaction occurs via interactions with the nucleus and electron clouds of atoms. Reaction (7) is a schematic of how energy is absorbed by a species M and how the electrons can propagate the reaction (Reich and Stivala, 1971). Degradation caused by direct irradiation is often small compared to reactions of oxygen with radicals to create peroxy radicals. Little data exist for the degradation of Kel-F or Estane by  $\gamma$ -irradiation, but it is expected the greatest effect would be caused by exposure at low doses in an oxygen atmosphere (Overturf and LeMay, 1997; Gillen and Clough, 1989).

### 2.3.3 *Plastic Bonded Explosives*

At this time, no publications relating to  $\gamma$ -irradiation of PBXs (i.e., the explosive and polymer combined) have been noted.

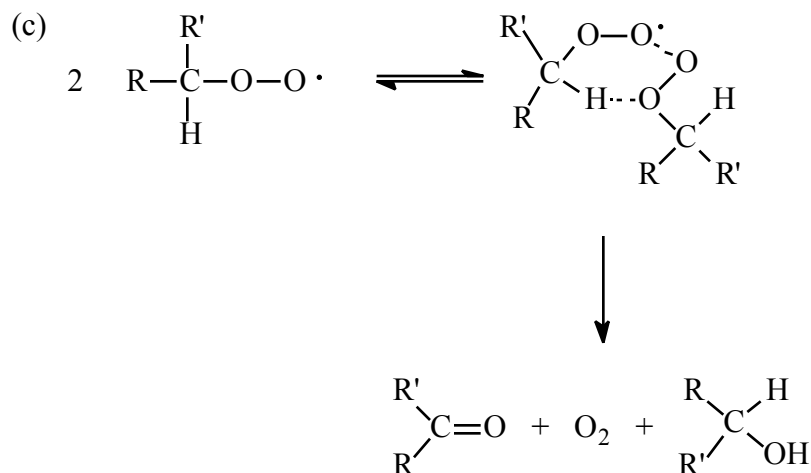
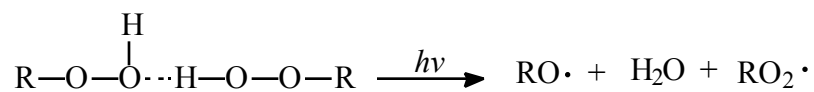
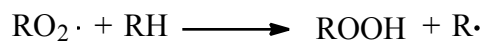
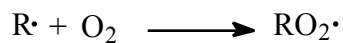
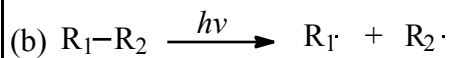
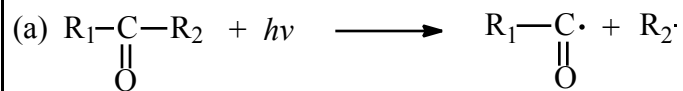
## 2.4 SOLVENT

### 2.4.1 *Explosives*

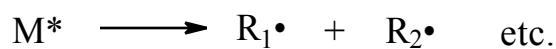
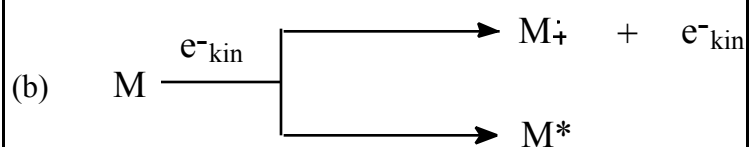
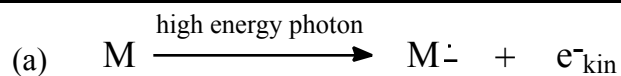
Degradation of the materials by a solvent can differ dramatically depending on the solvent used. TATB has an incredibly low solubility in any organic solvent, although it can be dissolved slightly in dimethyl sulfoxide (DMSO). However, TATB appears to be dissolved in some acids and bases although the TATB is actually degraded in the process. Sulfuric acid has been used to get TATB in solution for NMR analysis (Harris, 1979). Various bases (NaOH, KOH, Ba(OH)<sub>2</sub>, and NH<sub>4</sub>OH) have been used to provide soluble derivatives for a simple qualitative HE test (Harris, 1985). When TATB is reacted, a bright orange solution is seen. Other impurities form a bright red solution.

RDX can be degraded in water when exposed to UV light (Burten and Turley, 1995). Cooney, et al. (1989) did a kinetic study of the pH dependence on the

### Reaction (6)

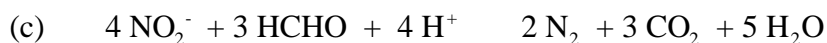
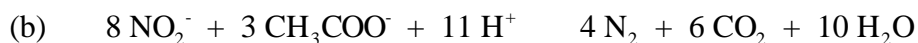
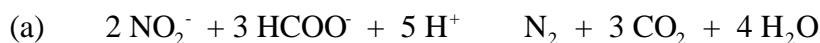


### Reaction (7)



decomposition of 3,7-dinitro-1,3,5,7-tetraazabicyclo[3.3.1]-nonane (DPT). DPT is a compound similar to RDX and HMX. The research was conducted mainly on DPT, but the authors related that their study could also be used to monitor the pH decomposition of RDX and HMX as they also contain N-nitro groups. Other researchers have used an alkaline hydrolysis reaction on RDX and HMX in order to decompose the compounds into smaller molecules, with the emphasis in more recent papers on removal of RDX and HMX from contamination sites (Urbansky, 1962; Heilman, et al., 1996; Zoh and Stenstrom, 1997). Alkaline hydrolysis of RDX and HMX produces  $\text{NO}_2^-$ ,  $\text{HCOO}^-$ ,  $\text{CH}_3\text{COO}^-$ ,  $\text{HCHO}$ ,  $\text{NH}_3$ ,  $\text{N}_2\text{O}$ , and  $\text{N}_2$  (Heilman, et al., 1996; Zoh and Stenstrom, 1997). The  $\text{NO}_2^-$  can be reacted with the various carbon sources ( $\text{HCOO}^-$ ,  $\text{CH}_3\text{COO}^-$ ,  $\text{HCHO}$ ) in a denitrifying anoxic biological process in order to make  $\text{N}_2$ ,  $\text{CO}_2$ , and  $\text{H}_2\text{O}$  (Zoh and Stenstrom, 1997). The balanced equations are shown in reactions 8a, b, and c (Zoh and Stenstrom, 1997).

### Reaction (8)

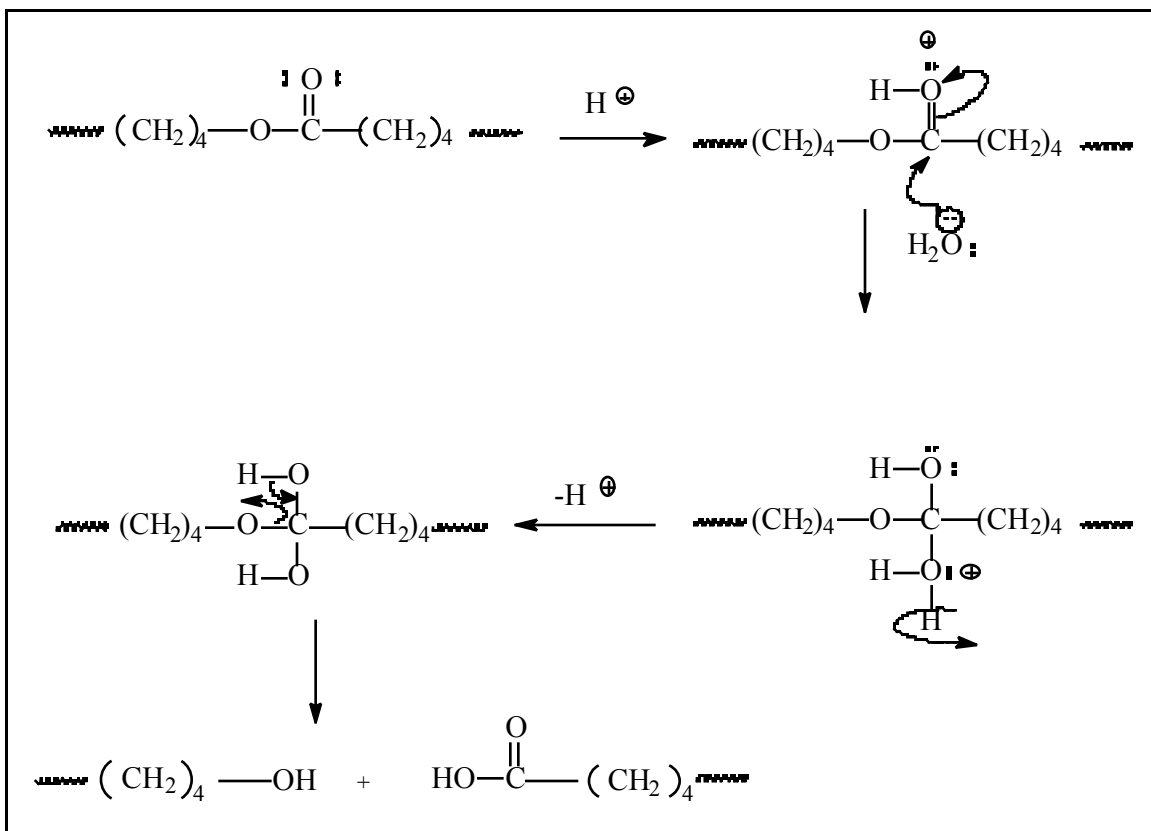


### 2.4.2 Polymers

Polymers may dissolve or possibly degrade when in organic solvents, but degradation can also be due to impurities present in the polymers. Huisman and van der Linden (1984) noted that the Estane polymer used for magnetic tape coatings was degraded by an HCl impurity. They demonstrated that the polyesterurethane was degraded in the presence of HCl because the HCl catalyzed the hydrolysis reaction of the ester bond and also caused a breaking of the urethane bond. However,  $\text{H}_2\text{SO}_4$  did not cause a similar degradation. Lightfoot and Russell (1998) have shown that Estane degradation is due to hydrolysis of the ester bond even in "dry" Estane, as it was found that water had adsorbed onto the Estane. Under high humidity conditions (and heat over several months), the degradation was more advanced. Figure 7 shows the mechanism for ester hydrolysis.

### 2.4.3 Plastic Bonded Explosives

At this time, no publications relating to solvent degradation of PBXs (i.e., the explosive and polymer combined) have been noted.



**Figure 7:** Possible Mechanism for Ester Hydrolysis

### 3. ANALYTICAL TECHNIQUES AND CHARACTERIZATION

#### 3.1 EXPLOSIVES

Explosives have been analyzed as individual components and as PBXs. This section concentrates on the individual explosives TATB, RDX, and HMX. Dobratz (1995) discusses various analytical methods used to measure the impurities in TATB after its synthesis. Yasuda (1972 & 1973) used TLC and GC to determine the impurities of TATB synthesis by using various solvent combinations because of TATB's insolubility (Dobratz, 1995). First, he used dimethyl sulfoxide (DMSO) (solubility ~70 ppm), then DMSO/H<sub>2</sub>SO<sub>4</sub> to purify the mixture. Later, Yasuda found that methanesulfonic acid would dissolve 800 ppm of TATB, so he combined H<sub>2</sub>SO<sub>4</sub> with methanesulfonic acid. Kayser (1983) developed a high performance liquid chromatography (HPLC) method for several explosives, including TATB, RDX, and HMX. The technique required a C-18 reverse phase packing with a UV detector set at 234 nm. The eluent used was a methanol/water mixture, set at a flow rate of 2.0 mL/min. HMX was not resolved completely in the explosive mixtures. Oxley, et al. (1995) also used HPLC and GC/flame ionization detector (FID) to analyze TATB. The HPLC conditions were very similar to Kayser's. For the GC, a fused silica Alltech 5-BP column was used (see publication for temperature program). Farber and Srivastava (1981) decomposed (pyrolyzed) TATB and used MS to monitor the products. Recently, Yinon et al. (1997) used electron ionization in tandem with mass spectrometry collision-induced dissociation (ESI-MS) to produce identifiable ESI-MS of explosives (TATB, RDX, and HMX). Saferstein, et al. (1975) used isobutane chemical ionization detection MS to analyze traces of explosives left at crime scenes.

Because TATB has such a low solubility in most solvents, there have been several methods used to analyze TATB as a solid and to characterize the TATB structure. Cady and Larson (1965) did optical and X-ray crystallography, the results of which have been included in most publications that attempt to determine the structure of TATB. They noted that TATB had some unusual features in the

crystallographic structure. Most notably, the C-C bond lengths in the ring were very long and thought to be due to inter- and intramolecular H-bonding. More recently, Wolff, et al. (1991) has done X-ray diffraction on several triaminotrinitrobenzenes, but not on TATB specifically. Dobratz (1995) discussed many characterization parameters for TATB. Gupta and Deopura (1970) used low frequency neutron spectroscopy to analyze TATB. XPS was done on TATB (Sharma, et al., 1982; Wang and Wittberg, 1989). Both noted that after exposure to X-rays or UV radiation that the spectra showed a loss of NO<sub>2</sub> in the exposed materials compared to the unexposed TATB. Britt, et al. (1981) used ESR to note the increase in radicals after TATB was exposed to UV radiation. Firish and Guse (1984) obtained Britt's ESR spectra only to dispute the radical predicted by Britt (1981). Firish and Guse (1984) used UV-visible, IR, Raman, and ESCA to characterize the TATB exposed to UV, but did not find any of these techniques helpful. NMR has also been used on TATB, but the solution NMR did not provide very much useful information because of the low solubility of TATB in organic solvents (Kayser, 1983; Wang and Wittberg, 1989; Clink, 1980).

Some of the most recent work was to use electron diffraction to explain the large second harmonic generation effect in TATB (Voight-Martin, et al., 1996 & 1997). Kunz (1996) used computational methods to determine the theoretical structure and electronic properties of TATB and RDX in order to explain the differences in sensitivity and stability. They noted one of the biggest factors affecting the sensitivity was the greater binding energy of TATB compared to RDX.

#### 3.2 POLYMERS

As polymers are unique macromolecular substances, they are analyzed by both traditional methods and methods developed particularly for the large molecules. The analysis of polymers can be limited because of low solubilities in organic solvents and not every molecule in a batch of polymer is the same; for instance, instead of an absolute molecular weight, the average molecular weight would be determined.

A good source for information to decide on the best analytical method to analyze

a polymer is the *Handbook of Instrumental Techniques for Analytical Chemistry* (Settle, 1997). Several chapters are devoted to polymer instrumental analysis. The traditional methods that can be used to analyze polymers are IR, NMR, X-ray, and MS. These methods are useful in defining the components of complex polymeric systems. However, the other methods were developed in order to understand the average size of the molecule and the performance of the polymer as a material.

The most common method to analyze molecular weight distribution is with size exclusion chromatography (SEC) and can be done on most HPLC systems. Usually an apparent molecular weight is determined, and if a calibration standard very similar to the polymer being analyzed is used, the absolute average molecular weight can be elucidated. Typically the column has several sizes of packing (or columns can be connected in series). One of the newer techniques developed to help calculate the molecular weight of various fractions from the SEC is to use matrix-assisted laser desorption ionization (MALDI). Molecular weight can also be determined absolutely on homopolymers by low angle laser light scattering. It is particularly helpful in identifying biopolymers and providing characterization on the intrinsic viscosity of a polymer. However, molecules must be larger than 10,000 g/mol for useful information. Other methods can be used to determine the viscosity, such as viscometry, ultracentrifugation, and osometry.

Mechanical properties of polymers are useful in determining the quality of freshly made polymers or of aged polymers. Thermal methods include DSC and thermogravimetric analysis (TGA). These methods, along with dynamic mechanical methods (methods that apply forces to the material in order to test material strength and flexibility) are useful to define the state of a polymer sample. These methods can be used to determine the glass transition temperature ( $T_g$ ), the melting point ( $T_m$ ), and degree of crystallinity.

Most of these methods have been applied to the polymers that have been used for explosion formulations. Estane 5701 was analyzed by IR, NMR, and DSC (Froix and Pochan, 1976). The goal of the research was to determine transitions in the polymer upon

heating. Variable temperature (140-500 K)  $T_1$  and  $T_2$  NMR relaxation experiments were run, but experiment detail was unclear. Initial  $T_g$  was 233 K, but after initial heating, the DSC curve showed many changes indicating that higher temperatures do strongly affect Estane quality. A unique method was tried by Matuszak (1981) on Estane 5703. They used FLAG in order to determine the loss of small amounts of  $H_2O$  and  $CO_2$  from the polymer upon heating. They did find  $CO_2$  elution from Estane over long periods of time and temperature. Chang et al. (1982) monitored changes in mechanical properties when aging polyisobutylene polyurethane. They found few changes in mechanical properties even after thermal aging and testing of hydrolytic stability.

SEC has also been used on polyester polyurethanes in order to determine changes in molecular weight upon degradation in organic solvent (Huisman and van der Linden, 1984). A Waters model 100 GPC was used with a  $\mu$ -Styragel column with a range of sizes from  $10^2$ - $10^6$  Å. The THF eluent required a flow rate of 2 mL/min and UV detector set at 254 nm. The unit was calibrated with polystyrene standards. A similar method was used on a polyester to determine hydrolytic degradation (Chang and Kennedy, 1982). Again, a  $\mu$ -Styragel column (HT) was used with a mass range of  $10^3$ - $10^5$  Å. The solvent used was hexafluoroisopropyl alcohol with a flow of 1.0 mL/min and a standard of polymethylmethacrylate.

For Kel-F, most of the focus was on change in the crystallinity. Overturf (1997) reported several properties based on XRD and DSC. Crystallinity can vary in Kel-F (up to 25% of the material) even before being exposed to any type of aging because of various factors in the processing of the material. Varying crystallinity can greatly affect the mechanical properties. DSC showed these variations. A typical  $T_g$  reported was 31°C. Kel-F is soluble in acetone, butyl acetate, THF, methyl ethyl ketone, and methyl isobutyl ketone. Hoffman, et al. (1989) also monitored the changes in crystallinity of Kel-F and found similar results.

NMR analysis has been performed on Kel-F, but mainly on the  $^{19}F$  isotope. Solution  $^{19}F$  NMR was done by Naylor (1960) with a 30 MHz magnet (Overturf and LeMay, 1997).

Solid-state  $^{19}\text{F}$  NMR (338.7 MHz) with magic angle spinning (MAS) was done in 1987 by Maciel (1987). They ran into difficulty due to the strong dipolar  $^{19}\text{F}$ - $^{19}\text{F}$  interactions and overcame the broadening from this by spinning at very high speeds (17 KHz). It was felt that this method could determine crystalline and amorphous character by noting differences in the relaxation behavior, but no follow up work has been published.

### 3.3 PLASTIC BONDED EXPLOSIVES

Since PBXs contain an explosive, a polymer, and sometimes stabilizers and plasticizers, analysis of the components together can be complicated. Most of the methods concentrate on using the HPLC or DSC to determine contamination or degradation of polymers. Mechanical strength and explosive properties can also be observed before and after aging.

Hoffman, et al. (1981) used HPLC (SEC specifically), DSC, and mechanical properties (shear storage modulus, shear loss modulus,  $T_g$ ) to determine the degradation of Kel-F and Viton A in the explosives PBX-9502 and LX-10-1. They found little degradation of Kel-F and PBX-9502 using these methods. They followed up this work by looking into the crystallinity changes in Kel-F using mainly DSC when thermally aging Kel-F (aging occurred between 23 and 74°C) (Hoffman, et al., 1989). Breithaupt (1978) looked at thermally aged RX-03-BB (a PBX of TATB and Kel-F 800) using tensile and maximum compression data, densities, DSC, and SEM. The data suggest an increased crystallinity in the samples as well as some small cracks and possibly debonding of the Kel-F from the surface of the crystal. This conclusion may explain some slight changes in density and mechanical properties in the aged samples. However, no chemical degradation mechanisms were presented. Myers (1977 & 1979) also tested the stress, strain, and density changes in aged coupons of X-0219 and PBX-9502 (essentially the same material) aged at temperatures between ambient and 100°C and found that changes started to occur at 100°C. The changes in the coupons were not related to changes in explosive properties. Skidmore, et al. (1998) did relate the explosive properties to the changes in mechanical properties.

Although they found similar changes in the PBX-9502 mechanical properties upon thermal degradation, there were few changes in explosive characteristics (Skidmore, et al., 1998). The authors concluded that PBX-9502 was an extremely stable PBX.

The exception in the analysis of a PBX comes from Clink (1983). He used  $^{13}\text{C}$  NMR on the Estane in RX-26-AF after extracting the Estane with acetone. He found that the Estane degraded in the samples aged in air but not in the samples aged in helium. The RX-26-AF used in this study contained no stabilizer.



#### **4. SUMMARY**

In summary, the PBXs made with TATB/Kel-F 800 have been found to be extremely stable even though some minor degradation has been noted in TATB and Kel-F 800. Something does happen to TATB when exposed to UV irradiation, but what happens still has not been determined. Kel-F 800 does undergo changes in crystallinity due to thermal degradation. RDX and HMX formulations with Estane are not as stable as the TATB formulations with Kel-F. As RDX and HMX are more sensitive even before aging than TATB, their use has been limited in PBXs. Estane is used with these explosive materials because of its mechanical properties, but does appear to go through significant hydrolytic degradation when exposed in some fashion to water, particularly if in HCl. Future work will focus on TATB degradation under irradiation as the literature is contradictory as to exactly what is happening with the material. Future work will also focus on the stabilizers and plasticizers that are incorporated into explosives as little is known about their degradative role in the PBX.



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