

# A SURVEY ON THE CYCLOTETRAMETHYLENE TETRANITRAMINE (*HMX*)

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Cyclotetramethylene tetranitramine (1,3,5,7-tetranitro-1,3,5,7-tetrazacyclo-octane) which has been classified as high explosive, a source of high chemical energy, falls into polynitramine group of the nitramines. It is also known as octogen and *HMX*. It is one of the most powerful explosives having high density (1.9 g/cc), high melting point (281°C) and high velocity of detonation (9100 m/sec). It has slightly higher energy than *RDX* and therefore, used where a maximum energy is required by limited dimensions of charge. Because of its resistance towards heat, it has become the nucleus of research for thermally stable compositions. It has been used in number of binary mixtures in conjunction with *TNT*, *RDX*, *TNB* etc. It forms the main constituent in certain plastic bonded explosives (*PBX*). In the present review attempt has been made to cover the available literature on *HMX*.

## SYNTHESIS OF *HMX*

Towards the end of last century Henning<sup>1</sup> started nitration of hexamine with nitric acid and later on Hertz<sup>2</sup> and Hale<sup>3</sup> carried out nitration of hexamine to get cyclotrimethylene trinitramine (*RDX*). During World War-II various modifications<sup>4-6</sup> were tried to increase the yield of *RDX* by using ammonium nitrate alongwith nitric acid and acetic anhydride. *RDX* some times contained a higher homologue viz *HMX*. The latter compound was isolated and synthesised by nitrating hexamine under different conditions than for *RDX*. After World War-II nitrolysis of hexamine was carried out by various workers<sup>7-10</sup> using acetic anhydride, ammonium nitrate and nitric acid and several products e.g. *RDX*, *DPT* (Dinitropenta methylene tetramine), *PHX*-(1-acetoxy-methyl 3,5,7-trinitro, 1,3,5,7-tetrazacyclo-octane), *QD* (Octahydro-1-acetyl-3,5,7-trinitro-*s*-tetrazine), *HMX* etc. were isolated under different set of experimental conditions. It was also observed that *DPT* can be converted to *HMX*.

A method for getting fair yield of *HMX* was reported<sup>11</sup> by the simultaneous addition of solution of ammonium nitrate in nitric acid and acetic anhydride to the hexamine in acetic acid at 50°C. Yield of *HMX* obtained was about 40-50%. A patent<sup>12</sup> for synthesis of *HMX* was taken in which the said compound was obtained by treating 3,7-dinitropentamethylene tetramine with 96% sulphuric acid. The efforts to get good yield of *RDX* or *HMX* were continued and several more compounds<sup>13-14</sup> were detected and isolated in the process of nitration of hexamine. It was noticed that *HMX* can be made from *PHX* which in turn can be synthesised from *DPT* an intermediate stage in the preparation of *HMX*. The effect of proportion of reactants, temperature and concentration of the ingredients on the yield of *HMX* and *RDX* was also studied<sup>15</sup>.

To get *HMX*' exclusively, many workers<sup>16-18</sup> performed nitration of hexamine with ammonium nitrate in nitric acid and acetic anhydride under different set of conditions reporting yield of *HMX* upto 60-70%. A good yield of *HMX* (about 85-90%) was reported<sup>19-21</sup> by using three feed two stage methods. In the first stage hexamine was nitrated to *DPT* which in turn was converted to *HMX* in the second stage as depicted below.

|                                                                             |                                                                            |                                                   |                                                              |                                             |
|-----------------------------------------------------------------------------|----------------------------------------------------------------------------|---------------------------------------------------|--------------------------------------------------------------|---------------------------------------------|
| Little ( $CH_2O$ ) <sub>x</sub><br>or $BF_3$<br>+ Trace $Ac_2O$<br>+ $AcOH$ | $44 \pm 2^\circ C$                                                         | Reaction mixture<br>at the end of<br>1st addition | $44 \pm 2^\circ C$                                           | <i>DPT</i> + spent<br>nitrolyzing<br>medium |
|                                                                             | 1st addition 15 min<br>Hexamine/ $AcOH$<br>+ $Ac_2O$<br>+ $NH_4NO_3/HNO_3$ |                                                   | 1st aging<br>15 min.                                         |                                             |
| $44 \pm 2^\circ C$                                                          | Reaction mixture                                                           | $44 \pm 2^\circ C$                                | <i>HMX/RDX</i>                                               | $110^\circ$                                 |
| 2nd addition<br>15 min.<br>$Ac_2O$<br>+ $NH_4NO_3/HNO_3$                    | at the end of<br>2nd addition                                              | 2nd aging<br>60 min.                              | + other<br>products<br>+ spent<br>nitroly-<br>zing<br>medium | $H_2O$<br>Reflux<br>&<br>filter             |
|                                                                             |                                                                            |                                                   |                                                              | <i>HMX/RDX</i><br>& other<br>byproducts     |



have been developed for detection and separation of *RDX* and *HMX* from each other to get pure compounds. In 1951, S. Epsteine *et al.*<sup>32</sup> carried out homogenous hydrolysis of *RDX* and *HMX* in aqueous acetone with 0.6 *N*/*N*NaOH. Owing to the difference in rate of hydrolysis calibration curve could be drawn up from which the percentage of *HMX* and *RDX* could be measured.

Chromatographic methods for detection and separation of *HMX* in hexogen were reported<sup>33-34</sup>. Similar studies were also done using T.L.C. techniques<sup>35-36</sup>. Gas chromatographic technique<sup>37</sup> was also used for the detection of *RDX* in *HMX*. Colorimetric methods<sup>38-39</sup> for determination of *HMX* in mixtures were studied. It was also determined with the help of potentiometric<sup>40</sup> titrations. An I.R. spectrophotometric<sup>41</sup> method was developed to detect *RDX* in *HMX*. A thin layer chromatographic method<sup>42</sup> for determining the *HMX* as contaminant in waste water arising from various explosive operations has also been reported. In 1957, Werbin<sup>43</sup> studied the I.R. spectra of *HMX* and *RDX*. He observed that prominent bands at 1283  $\text{cm}^{-1}$  of *HMX* and 1275  $\text{cm}^{-1}$  of *RDX* were most likely associated with *N*-NO<sub>2</sub> groups. The majority of bands were common to both *HMX* and *RDX* but difference occurs only below 1000  $\text{cm}^{-1}$ .

The complexes<sup>44-47</sup> of *HMX* with the dimethylformamide, *N,N*-dimethylpropionimide *N,N*-diethylacetamide, butyrolactone, cyclopentanone etc. were studied. This was used as the basis of estimation of *HMX* in admixture with *RDX*. Thatcher<sup>48</sup> described a method for the separation of *HMX* from its mixture with *RDX*. He dissolved the mixture in dimethylsulphoxide/water at 90°C, and was cooled rapidly with stirring. The solid *HMX* was filtered off. The filtrate was treated with water and cooled thrice to produce *HMX*. From the final filtrate *RDX* was recovered. James Watter<sup>49</sup> separated the *HMX* from *RDX* by forming complex with dimethylformamide or acetamide etc. and ultimately *HMX* was recovered by decomposition of addition compound with water or acetone or methyl alcohol etc. Dawson Ralph<sup>50</sup> also reported a method for separation of *RDX* and *HMX* with cyclopentanone. Scullion *et al.*<sup>51</sup> reported the method of detection of *HMX* in *RDX* by making the complex with dimethylformamide and then hydrolyzing it with hydrochloric acid followed by successive addition of copper sulphate, ammonium hydroxide, carbon disulphide and benzene. The presence of *HMX* is indicated by brown colour of copper dimethyldithiocarbamate in benzene. Walter Selig<sup>52</sup> has studied the adducts of *HMX* with benzene and naphthalene derivatives. A thermo chemical<sup>53</sup> investigation of complex formed by *HMX* and *DMF* was carried out by Charles Lenchitz and Rodolph Velicky.

Steneley Semel<sup>54</sup> has reported a spot test for the detection and differentiation of *RDX* and *HMX*. The sample was taken in conc. H<sub>2</sub>SO<sub>4</sub> and quinalizarine reagent was added, the colour change occurs after 20 min. *RDX* yields a light yellow colour and *HMX* yields a blue colour but the blue colour of *HMX* turns to yellow after half an hour. Amas & Yellop<sup>55</sup> reported modified method for identification of *HMX* with thymol and H<sub>2</sub>SO<sub>4</sub>, *HMX* gave a pale blue green colour at 100°C.

Walter Selig<sup>56</sup> carried out non-aqueous potentiometric titration of *RDX* and *HMX* as acids with tetrabutyl ammonium hydroxide in solvents dimethylformamide, cyclohexanone etc. and estimated the amount of either of it in the mixture. Fauth *et al.*<sup>57</sup> titrated *RDX* and *HMX* potentiometrically with tetrabutyl ammonium hydroxide in number of solvents e.g. pyridine, piperidine, ethylene diamine, 1.4 dioxan, tetrahydrofuran etc. Sinha *et al.*<sup>58</sup> also carried out the analysis of *HMX*/*RDX* by non-aqueous potentiometric titration. Gutamacher & Selig<sup>59</sup> determined quantitatively *HMX* by reducing it with chromous chloride in dimethylformamide and hydrochloric acid solution. Excess of chromous chloride is back titrated with ferric ammonium sulphate using phenosafranine as indicator. Norwitz George carried out a semi-micro spectrophotometric<sup>60</sup> determination of *RDX* and *HMX*. Martel *et al.*<sup>61</sup> used a polarographic method for detection of *HMX* and *RDX* in mixtures.

#### PROPERTIES OF HMX

Octogen (m.p. 276  $\frac{1}{2}$  81°C) is a white crystalline substance. It exists in four polymorphic forms. It is non-hygroscopic and practically insoluble in water. Its solubility in various organic solvents<sup>62</sup> has been given in Table 1 and its specific heat at different temperatures is reported in Table 2.

TABLE 1

SOLUBILITIES<sup>62</sup> OF OCTOGEN IN GRAMS/100gm OF SOLVENTS  
AT TEMPERATURE(S)°C

| Solvent             | 30°   | 50°    |
|---------------------|-------|--------|
| Acetone             | 2.78  | 3.83   |
| Nitrobenzene        | 0.174 | 0.257  |
| Dioxane             | 0.183 | 0.270  |
| Acetic acid         | 0.033 | 0.0657 |
| Pyridine            | 1.576 | 2.034  |
| Cyclohexanone       | 3.06  | 3.801  |
| Ethylformate        | 0.33  | 0.56   |
| Ethylacetate        | 0.32  | 0.43   |
| Methyl ethyl ketone | 1.403 | 1.73   |
| Nitromethane        | 1.04  | 1.59   |
| Toluene             | 0.011 | 0.016  |

TABLE 2

SPECIFIC HEATS<sup>63</sup> OF OCTOGEN AT DIFFERENT  
TEMPERATURE(S)°C

| Temp.<br>(°C) | Cal/gm/°C |
|---------------|-----------|
| -75           | 0.153     |
| 0             | 0.225     |
| 25            | 0.248     |
| 50            | 0.266     |
| 75            | 0.282     |
| 85            | 0.288     |
| 90            | 0.290     |
| 100           | 0.295     |
| 125           | 0.307     |

Vapour pressure and heat of sublimation have also been determined by Rose<sup>64</sup> et al in 1969. The study on the surface chemistry of *HMX* was also carried out by many workers<sup>65-68</sup>.

Figure 2—Polymorphic forms of *HMX*: (A)  $\alpha$ -*HMX*; (B)  $\beta$ -*HMX*; (C)  $\gamma$ -*HMX* and (D)  $\delta$ -*HMX*.

### Polymorphic Forms of *HMX*

It exists in four polymorphic forms. The characteristic properties of polymorphs are given in Table 3.

TABLE 3  
PROPERTIES<sup>25, 27</sup> OF POLYMORPHIC FORMS OF *HMX*

|                                                                    | $\alpha$    | $\beta$ | $\gamma$    | $\delta$  |
|--------------------------------------------------------------------|-------------|---------|-------------|-----------|
| Specific gravity                                                   | 1.87        | 1.96    | 1.82        | 1.77      |
| Stability                                                          | Meta stable | Stable  | Meta stable | Unstable  |
| Shape of crystal                                                   | Needle form | Equant  | Triangular  | Hexagonal |
| Specific heats at 25°C cal. K <sup>-1</sup> , g <sup>-1</sup> (cp) | 0.248       | 0.243   | 0.265       | 0.313     |
| Relative insensitivity to impact kg/fall height (cm)               | 1/20        | 5/15    | 1/20        | 1/10      |

### Preparation of Polymorphic Forms

Preparation of four polymorphic forms was reported by McCrone<sup>69</sup>, Licht<sup>70</sup> and Bedard<sup>71</sup> etc. All the forms can be prepared by same solvent with different rate of cooling or with different solvents under different set of conditions.

$\alpha$ -HMX : It can be obtained by dissolving  $\beta$ -HMX in boiling 70% nitric acid and cooling slowly. The separated crystals are washed with water and dried at 100°C.

$\beta$ -HMX : It can be obtained by cooling hot saturated solution of HMX in acetonitrile or acetone.

$\gamma$ -HMX : (i) It is prepared by dissolving  $\beta$ -HMX in boiling cyclohexanone and pouring the solution into a mixture of ethyl alcohol and water. The separated crystals are washed with ethyl alcohol and dried. (ii) It can also be prepared by dissolving HMX in warm 50% acetic acid followed by rapid cooling in ice bath.

$\delta$ -HMX : It can be prepared by dissolving HMX into boiling cyclohexanone and pouring the solution into paraffin oil at 150°C. The mixture is filtered hot and crystals washed with petroleum ether and dried 100°C. Walter Selig<sup>72</sup> also described a method for preparation of  $\delta$ -HMX stable at ambient temperature.

#### Conversion to $\beta$ -HMX

Synthesised HMX containing all the four isomers was brought to a slurry in acetone-water mixture<sup>73-74</sup>. The slurry was refluxed and cooled to 25°C and it was seeded with  $\beta$ -HMX. Then water was added to the slurry and mixture was heated to remove the acetone, cooled to 30-40°C and filtered under vacuum to get  $\beta$ -HMX.

#### Crystallographic Studies

All the polymorphic forms were studied by X-ray diffraction<sup>75-77</sup> ultra-violet and visible absorption spectra<sup>78</sup>. Microscopic studies<sup>79</sup> of HMX were also undertaken. The crystal structure of  $\beta$ -HMX has been investigated by neutron diffraction<sup>80</sup> method. Out of the four forms of HMX,  $\beta$ -form is the most stable at room temperature and is also insensitive to impact in comparison to its other forms. It is used in explosive mixtures. The presence of other polymorphic forms even in traces make the  $\beta$ -form sensitive. Therefore, other form should be converted to  $\beta$ -form or should be eliminated necessarily. Physicochemical properties<sup>81</sup> of HMX were also studied by Maycock *et al.* They measured the electric conductance in the single crystal, pelleted  $\beta$ -HMX and polycrystal  $\delta$ -HMX. The effect of UV radiation<sup>82</sup> was also studied. The effect of nuclear radiation<sup>83</sup> on the HMX has been reported.

#### Chemical Properties

The structure of HMX is shown in Fig. 3

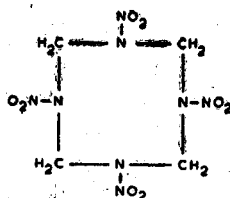


Fig. 3—Structure of HMX

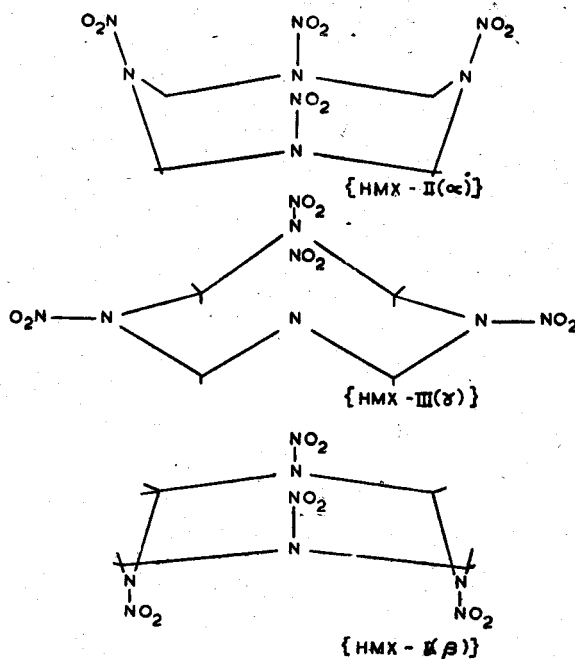


Fig. 4—Conformational structure of HMX.

Conformational structure of polymorphic forms of HMX as suggested by Wright *et al.*<sup>34</sup> are given in Fig. 4.

Little work has been done on the chemical properties of *HMX*. But it is reported in literature that it has almost similar properties as *RDX* except that *HMX* is not easily decomposed by alkaline hydroxide as shown in Table 4.

TABLE 4  
COMPARATIVE PROPERTIES <sup>25,63,112A</sup> OF *RDX* & *HMX*

|                                                                          | <i>RDX</i>                    | <i>HMX</i>                      |
|--------------------------------------------------------------------------|-------------------------------|---------------------------------|
| Crystal density                                                          | 1.8                           | 1.9                             |
| V.O.D.                                                                   | 8400 m/sec                    | 9100 m/sec                      |
| F of I                                                                   | 70                            | 52                              |
| Melting point (°C)                                                       | 203                           | 281                             |
| Ignition temp. (°C)                                                      | 213                           | —                               |
| Polymorphic forms                                                        | Nil                           | Four forms                      |
| Hardness mohs scale                                                      | 2.5                           | 2.3                             |
| Vacuum stability test at 120°C (cc gas evolved from)<br>5 g sample/40 hr | 0.9 cc                        | 0.45 cc                         |
| Solubility in 100 gm <i>TNT</i> at different temp.                       | 4.5 to 8.2 g                  | 0.4 to 0.7 g.                   |
| Reaction with alkalis                                                    | Easily decomposed             | Not easily decomposed           |
| Reaction with $H_2SO_4$                                                  | Librates $HNO_3$ rapidly      | Librates $HNO_3$ slowly         |
| Complex formation                                                        | Does not form complex         | Forms complexes                 |
| Solubility in the organic solvents                                       | More                          | Less                            |
| Heat of formation                                                        | —96 cal/g<br>—21.3 K cal/mole | —60.5 cal/g<br>—17.1 K cal/mole |
| Detonating pressure (K bars)                                             | 347                           | 393                             |

#### Explosive Properties<sup>68</sup>

1. Brisance by sand test 54.4 to 60.4 g sand crushed vs 48 g for *TNT*.
  2. Confined "cook off" Temperature 210°C.
  3. Explosion temperature 306° in 10 sec 327° in 5 sec and 380° in 0.1 sec with no cap used.
  4. Friction pendulum test Explodes with steel shoe unaffected by fibre shoe. Heat of explosion calcd with  $H_2O$  liquid 1356 and calcd with  $H_2O$  gas 1222 cal/g.
  5. Impact sensitivity Bur Mines app, 2 kg wt. 32 cm for 20 mg sample; B. A. app. 2 kg wt. 9 inches for a 23 mg sample vs 95 & 14+ as comparable values for *TNT*.
  6. Power By Ballistics Mortar 15% *TNT*, by Trauzl test 145% *TNT*.
  7. Sensitivity to initiation Minimum detonating charge required for maximum brisance is 0.30 gms of lead azide.
- Thermal stability *HMX* is more stable than *RDX* as indicated by vacuum stability and explosion temp test. The 150 vacuum stability test shows *HMX* to be comparable to *TNT* and ammonium picrate in thermal stability.
9. Vacuum stability test cc gas evolved/40 hrs/5g sample—0.37 at 100°, 0.45 at 120° and 0.62 at 150° meters.
  10. Velocity of detonation 9124 /sec.

### Thermal Decomposition

The thermal behaviour of  $\beta$ -HMX has been investigated by many workers<sup>85-88</sup>. Maycock<sup>89</sup> studied the decomposition of  $\delta$ -HMX. Recently Takaria & Okazaki<sup>90</sup> studied thermal decomposition of HMX and found that the rate of decomposition of HMX increases rapidly at about 250° whereas RDX does not decompose appreciably upto 190°C. W. John<sup>91</sup> described two new methods for determining the stability of explosive compositions of RDX and HMX with TNT.

### HMX in Explosive and Non-Explosive Mixtures

HMX is a very sensitive compound and it can be used as bursting explosive after desensitization. To reduce its sensitivity, it is phlegmatized with wax, resin, TNT and with other polymeric compounds. Linder<sup>92</sup> studied the effect of waxes and other desensitizing materials on the initiation and propagation of explosions in HMX. He also found that desensitization is not merely a thermal sink but it acted as a transit thermal insulator, which prevents conduction of heat from one explosive crystal to another. Charles E. Macknight<sup>93</sup> also collected the sensitivity data which show that coating with lead stearate can desensitize the HMX enough to reduce or remove the hazards involved in handling. For making HMX safely compacted material, Etat Francis<sup>94</sup> reported a method in which solution of polyvinyl acetate and dibutyl phthalate in ethyl acetate was added dropwise to the agitated suspension of HMX and little graphite in water at 80°C. Afterwards it was filtered and dried to yield coated particles. Taker Toshio<sup>95</sup> prepared easily mouldable composition by mixing HMX with the synthetic and natural wax. They<sup>96</sup> have also mixed HMX with polyester, epoxy or polysulfide resin containing hardeners and accelerators to get explosive having good mechanical strength and processibility.

Wright<sup>97</sup> patented the method for the preparation of explosive moulding powder of HMX. Leake<sup>98</sup> developed a method to recover HMX from the plastic bonded explosive. Walter Selig<sup>99-108</sup> has made valuable contribution in the field of plastic bonded explosive of HMX.

### Binary Explosive Mixtures Containing HMX

Kegler et al<sup>109</sup> studied the comparative properties of RDX/TNT and HMX/TNT (65 : 35). The effect of change in the explosive composition, density and diameter of the charge upon the detonation velocity were determined by them. HMX was found more effective than RDX in increasing the density of charges and velocity of detonation. Thermal stability of HMX/TNT mixtures were also studied. Castable mixtures of HMX<sup>110-112</sup> with the different mixtures of RDX, TNT, TNM, TNB and CE were also prepared and studied for low viscosity and increased detonation rate. The comparative data of binary explosive mixtures is given in Table 5. It shows that binary mixture containing HMX (octol) has higher density, velocity of detonation and detonation pressure.

TABLE 5  
HIGH POWERED MIXED EXPLOSIVES<sup>113A</sup>

| Designation   | Composition    | Density<br>g/cc | Detonation<br>velocity<br>(km/sec) | Detonation<br>pressure<br>(K bars) |
|---------------|----------------|-----------------|------------------------------------|------------------------------------|
| Amatol        | 50 TNT/50 AN   | 1.55            | 6.3                                | —                                  |
| Composition B | 40 TNT/60 RDX  | 1.70            | 7.9                                | 285                                |
| Cyclotol      | 25 TNT/75 RDX  | 1.75            | 8.2                                | 320                                |
| Octol         | 25 TNT/75 HMX  | 1.82            | 8.4                                | 340                                |
| Pentollite    | 50 TNT/50 PETN | 1.67            | 7.4                                | 245                                |

### Detonics

Quite a lot of work has been done on the explosive and detonation characteristics of HMX. Robertson<sup>113</sup> studied its sensitivity to impact by oscillographic method. Cachia<sup>114</sup> studied initiation by shock by introducing a metal wafer between two explosive pellets. Griffith<sup>115</sup> studied the mechanism of burning to detonation in HMX. Bobolev et al<sup>116</sup> reported a method for calculating the initial

temperature of hot centres for the shock initiation. The results obtained were in good agreement with the experimental values. Taylor<sup>117-118</sup> studied the burning of *HMX* by convective mechanism. He also studied the melting stage in the burning of explosive. Karpukhin<sup>119</sup> studied the effect of phlegmatizers such as stearic acid, paraffin bees wax in amounts of 1-15% on excitation and development of detonation on impact. Bruchman<sup>120</sup> reported the theoretical calculation of hot spot initiation in *HMX*. Afonina et al<sup>121</sup> studied the method of evaluating the tendency of *HMX* to undergo the transition from burning to detonation. Sinclair<sup>122</sup> determined effect of pressure on the auto ignition of *HMX*. Phung Tere<sup>123</sup> studied the initiation by high energy electrons which has very important conclusions. Products of detonation were also studied by calorimetric methods<sup>124-125</sup>.

#### USES OF *HMX*

As *HMX* is one of the most powerful explosives. It is used with various organic and inorganic compounds for getting high energy compositions for number of end effects. It may find application in propellants<sup>123-128</sup>, smokeless propellants<sup>129</sup>, rocket propellants<sup>130-131</sup>, temp. resistant-propellant<sup>132</sup>, rocket propellant granules<sup>133-134</sup> oxidizer<sup>135</sup>, heat resistant coating agent<sup>136-137</sup>. Heat stable compounds<sup>138</sup>, flexible explosive<sup>139-140</sup>, compressible explosive<sup>141-142</sup>, aerosol cloud formations<sup>143</sup>, plastic bonded explosive<sup>144-145</sup> and also in gelled slurry explosive<sup>146</sup>.

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