Metal-Fluorocarbon-Pyrolants: III. Development and Application of Magnesium/Teflon/Viton (MTV)

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Summary

The development and application of pyrotechnic payloads based on magnesium, Teflon® and Viton®, so-called MTV is reviewed. MTV is applied in decoy flares, tracking flares, countermeasure torches, base bleed units, tracer units, igniters, solid rocket propellants, RAM propellants, incendiary devices and signaling applications.
For Parts I and II see Refs. 12 and 65.

1 Introduction

One of the most versatile compositions applied in either military and technical pyrotechnics is a mixture based on **M**agnesium (Mg), **T**eflon®** (polytetrafluoroethylene (acr. PTFE) $(-C_2F_4-)_n$) and **V**iton® (hexafluoropropene-vinylidenfluoride-copolymer $(-C_5H_3F_7-)_n$), so called **MTV.** Although many investigators have addressed single features of this system[1–14], so far no comprehensive review on this important area of pyrotechnics exists. Thus the aim of the present article is to concentrate the existing data on the application of MTV in military and civilian pyrotechnics.

2 Development

It is assumed that the development of the MTV pyrolant system occurred sometimes in the mid 1950s after large-scale accessibility of then discovered polytetrafluoroethylene (PTFE) of which the mass production had started in 1946. This assumption is based on a classified reference dated back to 1958[15] found as well in Ref. 16 as on disclosures made at China Lake installation in 1957 and 1958 which have not been released for public access until 1973[17] and 1997[18] and a disclosure made in 1956 at Rockville also not released for public access until 1964[19]. For about ten years the realm of governmental secrecy surrounded MTV and its application as an IR decoy material, because MTV showed and still shows superior performance in terms of specific infrared radiant intensity E_λ $[J \cdot g^{-1} \cdot sr^{-1}]$ compared to many other pyrolant systems. In 1964 Shidlovsky[20] is believed to be the first to "propose" the application of pyrotechnics based on stoichiometric mixtures of magnesium and PTFE. Shidlovsky also gave a rough estimate for the specific combustion enthalpy of a stoichiometric mixture with $\xi(Mg) = 0.32$ of about $9.62\ kJ \cdot g^{-1}$. This value is in good agreement with the experimental value found for the heat of explosion ($9.4\ kJ\ g^{-1}$) determined by Peretz[1]. In 1965 the applicability of fluorocarbons, mainly poly(tetrafluoroethylene), to act as oxidizers in propellants together with metallic fuels such as magnesium and/or aluminium was proposed in a disclosure by Eldridge but was not released for public access until 1975[21]. By 1968 Ellern cites the application of magnesium-fluorocarbon compositions as IR decoy flare payloads in his textbook on pyrotechnics[22]. The application of MTV in retarding charges for rockets was proposed in a Swiss disclosure in 1968 and published in 1970[23].

The finding that a fluorocarbon such as Teflon® might act as an oxidizer was supposed to occur soon after its commercial accessibility was ensured. The reason for that assumption is that pyrolants based on metal/organohalogen systems were known as early as in World War I when the French Berger invented a mixture producing black smoke based on tetrachloromethane (CCl_4) and zinc dust (Zn)[66]. Since then research on infrared decoy flares aimed at compositions yielding much heat as well as lots of black carbon for improved emission in the infrared[24], the following substitution was very likely to be found:

$$\begin{array}{llll} 0 & -135.5 & 2\cdot(-415.1) & \\ 2Zn & +\,CCl_4 & \longrightarrow 2ZnCl_2 + C & \Delta H_R^{298} = -694.7\ kJ \quad (1) \\ \downarrow & \downarrow & \downarrow & \downarrow \\ 0 & -809.6 & 2\cdot(-1124.2) & \\ \mathbf{2Mg} & +\,\mathbf{(-C_2F_4-)_n} & \longrightarrow \mathbf{2MgF_2} + 2n\,\mathbf{C} & \Delta H_R^{298} = -\mathbf{1438.8\ kJ} \quad (2) \end{array}$$

Introducing magnesium and polytetrafluoroethylene instead of zinc and tetrachloromethane yields more than twice the heat of reaction than latter systems. PTFE thus acts as a fluorine source to serve exothermic fluorination of

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** Teflon (polytetrafluoroethylene) and Viton (hexafluoropropene-vinylidenfluoride-copolymer) are trademarks of DuPont.

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magnesium, a process which also has been proposed as chemical lasing system[25,26].

$$Mg_{(g)} + F_{2(g)} \rightarrow MgF_{(g)} + F + h \cdot v \quad (3)$$

3 Application of MTV

Comparable to black powder or magnesium/sodium nitrate ($NaNO_3$) pyrolants, MTV has found application in a multitude of areas covering countermeasures, tracking flares, tracers, igniters, incendiaries, propellants and many more due to its universal behaviour

In the following a brief survey of the main applications of MTV and its derivatives is given.

3.1 Decoy Flares and Tracking Flares for Aerial Gunnery

As discussed in the previous section, MTV was first applied as IR emitting payload in both decoy flares and shortly after it in tracking flares for aerial gunnery with then developed IR guided surface-to-air missiles. A detailed review on decoy flare compositions including MTV is given by the author in Ref. 24.

3.2 Tracking Flares for Missile Guidance Purposes

Derived from air gunnery training is the application of MTV as tracking flare for missile guidance in **s**urface-to-**a**ir-**m**issiles (SAM) and **a**nti**t**ank-**g**uided-**m**issiles (ATGM). Similarly as in countermeasure applications, MTV provides an intense IR emission in the short wavelength infrared region (2 – 3 μm) that can be tracked from the launch pad thereby helping to guide the missile. Tracking flares for guidance purposes must provide a constant level of incident radiation intensity at the detector. Therefore, such flares must deliver a continuously rising radiant intensity as the missile moves its way toward the target. Typical tracking flares comprise either a series of different compositions starting with nearly stoichiometric ratios in the beginning of the burning time and ending with fuel rich compositions at the end of the burning time[12] or payloads with an exponentially rising burning surface in case of a single composition when the missile has travelled a distance r to overcome the decrease of radiation intensity given by the square law r^{-2} as well as to compensate for atmospheric attenuation. For radio guidance purposes of the missile the MTV payloads in these applications must not yield any combustion products that interfere with the radio signal by means of scattering or absorption[27]. Typical burning rate enhancers such as metallic Zr powder[6], yielding hot ZrO_2 aerosol which was identified to interact with radio signals due to thermionic emission[28] must be excluded from such payloads. Likewise alkali metal and alkaline earth metal-based modifiers for MTV, such as sodium fluoride (NaF) and barium stearate ($CH_3(CH_2)_{16}CO_2Ba$)[29] compounds, may cause severe problems due to the partial ionisation of the metal.

3.3 ATGM Countermeasure Flares

Another countermeasure application of MTV is its use against line of sight (LOS) guided ATGMs. Some of the ATGMs use MTV tracking flares in order to provide a signal to be tracked by the operator (cf. Section 3.2). In order to confuse an operator wire-guiding an ATGM MTV, torches are ignited on a tank to provide two radiating sources in the field of view (FOV) of the operator. A mature design of such a countermeasure is the French GALIX 6-torch[30]. Although this technique is working quite well, modern ATGMs or SAMs work with narrower FOVs as well as frequency modulated solid-state lasers as radiation sources in order to discriminate torch-type countermeasures.

3.4 Base Bleed Application and Tracers

As missiles may have tracking flares, unguided munitions often apply tracer units in order to make the observation of the munition trajectory possible. Ramnarace proposed tracer compositions and suitable igniter compositions constituted from MTV. He also proposed modified MTV tracers comprising additional strontium nitrate ($Sr(NO_3)_2$) in order to provide a pink to deep red flame colour depending on the amount of strontium nitrate included in the composition[31].

Another area of application concerns base bleed purposes in artillery shells. Base bleed charges are pyrotechnic charges similar to tracers which are located at the shell base. They are supposed to reduce the drag coefficient of the shell by enhancing the air pressure in the wake of the shell due to the generation of gaseous combustion products thus reducing unpleasant aerodynamic turbulences. Typically, air pressure in the rear side of a shell travelling at Mach 2 is about 0.06 MPa. Suitable MTV payloads for base bleed charges comprise about 65% Mg[7]. The challenges in developing base bleed charges are the large set back forces (up to 18000 g), the high rate of spinning of the shell (200 – 300 s^{-1}), as well as the pressure drop upon firing of the shell which may cause quenching of the combustion[5].

3.5 Igniters

Upon combustion MTV yields large amounts of condensed products such as magnesium difluoride (MgF_2) and magnesium oxide (MgO) that may serve as heat transfer media for ignition purposes[1,32]. Radiation from formed carbon black adds to the heat transfer. Since highest caloric output of heat of combustion is attained between $\xi(Mg) = 0.44 - 0.5$[10–11], ignition charges with both optimum slag ejection as well as maximum black carbon formation will require stoichiometries with mentioned $\xi(Mg)$ values. MTV based ignition charges are very often made from the powdered constituents. Rentz proposes charges from magnesium, PTFE, Viton® and additional graphite serving as electrostatic desensitizer(33). With the development of vapour phase deposition techniques new pyrotechnic materials have become accessible. Keister proposes a device for destroying microcircuits which comprises electronic circuits covered with deposited layers from PTFE and magnesium(34). In view of this, Allford has proposed pyrotechnic igniter or propellant charges made by vapour deposition of magnesium on PTFE substrate(35). A rectangular PTFE tape (2 mm × 45 μm) having a Mg coating of ~16 μm burns with a burning rate of $r = 100\ m \cdot s^{-1}$ after insertion into a heat shrunk Viton® tube. Despite the performance of the freshly prepared material long term degradation of the magnesium coating by atmospheric constituents leads to deterioration of the igniter material. Graham et al. who observed that the degradation rate of a magnesium coating is approximately 3 μm/year improved this igniter material in several ways. By deposition of an oxygen diffusion barrier on the magnesium coating which may be of either alumina (Al_2O_3) or titanium(36) such igniters may be stored over long periods without notable deterioration. Applying porous PTFE substrates instead of non-porous material having an areal mass of ~25 to 75 $g \cdot m^{-2}$ enhanced the vivacity of the combustion result(37). The sheet material provided with defined pores and crazes on the surface will guide the flame spreading over it(38). When the sheet material is additionally covered with energetic materials such as nitrocellulose (NC) an enhanced gas production will be induced upon combustion(39).

3.6 Solid Rocket Propellants

As mentioned in Section 2, fluorocarbons have been very early identified as possible oxidizers in solid rocket propellants. Among other possible systems involving aluminium and zirconium as fuel as well as ammonium perchlorate and potassium perchlorate as oxidizers, one claimed composition consists of 51% PTFE, 15% Viton® 31% magnesium and 3% copper(II)-fluoride as burning rate modifier(21). A thermochemical calculation for this composition(40) yields large amounts of gaseous combustion products such as $MgF_{2(g)}$ (36%), $MgF_{(g)}$ (6%), HF (9%) and $Mg_{(g)}$ (1%). This is due to the high flame temperature, which was calculated to be ≈3208 K where said compounds are in the gaseous state (b.p. (MgF_2) = 2512 K) and thus contribute to the specific impulse.

3.7 RAM Propellants

The possibility of MTV to act as RAM propellants was proposed by Reed as early as 1983(41). He proposed fuel rich compositions $\xi(Mg) \approx 0.6 \pm 0.05$ in order to provide metal vapour as well as carbon fragments to be burnt with excess air supplied. The advantage of fluorocarbon/metal systems over classical metal/nitrate systems is the fact that the formed metal fluorides are in the vapour phase at the corresponding flame temperatures in contrast to the metal oxides and thus add to the specific impulse (b.p. (MgF_2) = 2512 K versus b.p. (MgO) = 3533 K)(42).

3.8 Incendiary Devices

The fact that MTV yields both a high flame temperature and large amounts of condensed products, and provides an intense IR emission enables this composition also for incendiary purposes. According to Waite(43), magnesium-Teflon® payloads comprising 50 – 80% Mg and 20 – 50% Teflon® are suitable for such an application. Many other incendiaries rely also on magnesium-Teflon® mixtures but may include additional fuels such as granular iron(44) and fuel type binders such as polysiloxane which provide hot slag due to silicon dioxide formation(45).

3.9 Signaling Applications

The high temperature attained upon combustion of MTV as well as the large amounts of condensed species make MTV also applicable as a signaling pyrotechnic composition(46) in both the infrared as well as the visible range. Cadwallader gives candle power values for payloads based on magnesium and cured polytrifluorchloroethylene(19).

3.10 Hypothetical applications

It is known that gaseous fluorine and gaseous, fluorine containing compounds (e.g. SF_6, C_4F_8, $C_{11}F_{20}$) may be applied as oxidizers in either propellant applications or submerged power plants such as **S**tored **C**hemical **E**nergy **P**ropulsion **S**ystems (SCEPS)(47). In addition, it has been reported to generate fluorine gas for hybrid propellant combustors by exothermal reaction from fluorocarbons and nitrosyl tetrafluoroborate ($NO^+BF_4^-$)(48). Thus it is not that far to extend the application of MTV to the generation of gaseous fluorocarbons for oxidizing purposes in the mentioned use. MTV is known to yield substantial amounts of fluorocarbons such as difluorocarbene (:CF_2) and tetrafluoromethane as well as hydrogen fluoride at $\xi(Mg) < 0.3$.

In Figure 1 a ternary diagram of magnesium, Teflon® and Viton® is given showing the application of certain stoichiometries for different purposes.

3.11 Miscellaneous

Aside from the pure application of the main ingredients in various pyrotechnic payloads a vast number of MTV blends does exist. In these formulations MTV is generally applied as a heat source. Many smoke compositions are based on MTV as heat source and additional aerosol sources such as

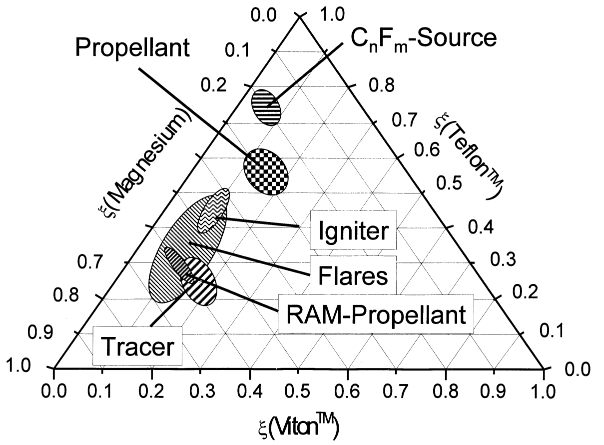

Figure 1. Ternary MTV diagram showing various applications.

red phosphorus[49] or aromatic compounds like polystyrene, naphthalene and hexachlorobenzene[50]. A high temperature composite propellant comprising 33% MTV and additional oxidizer barium nitrate ($Ba(NO_3)_2$) and coolant cyanuric acid ($C_3H_3N_3O_3$) has been disclosed by Hamrick[51].

4 Derivatives of MTV Pyrolants

With the discovery of PTFE to be a versatile oxidizer in energetic materials many compositions have been so far derived from MTV applying different metallic fuels (Al[9,14,52], Li[53], Ti[9,14,54], B[9], Zr[14] $CaSi_2$[55], Mg_4Al_3[8,14]). Truly exotic is a disclosure made by Dierolf who proposes to apply blends from PTFE, Viton®, mercuric oxide and **uranium** as high density rocket propellants[56]. In addition, numerous solid, viscous and even liquid fluorocarbons[57,58] such as Kel-F-wax[18], perfluoro-polyethers (PFPE)[52], perfluoro-paraformaldehyde[59] and TECNO-FLON®, polychlorotrifluoroethylene and LFC-1, which is a viscous fluoroelastomer based on 1,1,2,2,3,3-hexafluoro-1-propene-1,1-difluoroethene copolymer[60], have been applied especially in decoy flare applications. 1,1,7-Trihydro-dodecafluoroheptyl acrylate binder has been proposed for oscillating signal flare compositions based on magnesium[61]. Another fluorocarbon compound acting as both oxidizer and binder in pyrotechnics is 2,2,3,3,4,4,5,5-Octafluorohexane-1,6-diole. This compound can be processed similarly as HTPB (hydroxy-terminated polybutadiene) applying curative agents such as IPDI (isophorone diisocyanate) and has been proposed as fluorine source in magnesium or aluminum containing oscillating signal flares[62].

Recently poly(carbon monofluoride) ($(-CF-)_n$) better known as graphite fluoride has been discovered to act as a superior oxidizer compared to PTFE in Mg containing pyrolants due to the lower tertiary carbon C–F bond strength compared to the secondary carbon C–F bond strength in PTFE[63]. Thus, very high flame temperatures of > 5000 K may be attained[64,65].

5 Conclusion

Magnesium/Teflon®/Viton®-pyrolants are versatile materials for military and technical pyrotechnics. Although discovered nearly fifty years ago there are still remarkable developments which adapt applications of these highly energetic materials to present and future needs.

The thermochemical behaviour, such as combustion rate and mechanism will be addressed in part IV of this series.

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