

Theoretical and Applied Heat Engineering  
Теоретическая и прикладная теплотехника

EDN: DCSUKH

УДК 547

## Methods for Preventing Ferrocene Catalyst Migration into Solid Fuels

Ghulam R. Khabrat and Yuri I. Puzin\*

*Empress Catherine II Saint Petersburg Mining University  
Saint Petersburg, Russian Federation*

Received 02.07.2024, received in revised form 22.08.2024, accepted 28.08.2024

**Abstract.** Ferrocene compounds are among the most common solid fuel combustion speed catalysts, which have attracted the attention of scientists due to better combustion speed, ease of production, purity percentage and high efficiency. Due to their high migration, the main problem of these compounds is their migration during storage, which can reduce engine performance and cause subsequent risks. Various methods have been proposed to solve this problem, including branching, adding active groups and creating bulky compounds or strengthening intermolecular bonds, polymerization, excessive branching, etc., due to the high importance of the migration phenomenon. In the exploitation of solid fuels, this article introduces ferrocene-based combustion rate catalysts and briefly reviews methods to prevent their migration.

**Keywords:** ferrocene catalysts, combustion rate, solid fuel, ferrocene compounds, migration.

Citation: Khabrat Gh. R., Puzin Yu. I. Methods for preventing ferrocene catalyst migration into solid fuels. J. Sib. Fed. Univ. Eng. & Technol., 2024, 17(7), 888–909. EDN: DCSUKH



## Методы предотвращения миграции катализатора ферроцена в твердое топливо

Г. Р. Хабрат, Ю. И. Пузин

*Санкт-Петербургский горный университет  
императрицы Екатерины II  
Российская Федерация, Санкт-Петербург*

**Аннотация.** Соединения ферроцена являются одними из самых распространенных катализаторов горения твердого топлива, которые привлекли внимание ученых из-за лучшей скорости горения, простоты производства, чистоты и высокой эффективности. Из-за их высокой миграции основной проблемой этих соединений является их миграция во время хранения, что может снизить производительность двигателя и вызвать последующие риски. Для решения этой проблемы были предложены различные методы, включая разветвление, добавление активных групп и создание объемных соединений или укрепление межмолекулярных связей, полимеризацию, чрезмерное разветвление и т.д., ввиду высокой важности явления миграции. При эксплуатации твердого топлива в данной статье представлены катализаторы скорости горения на основе ферроцена и краткий обзор методов предотвращения их миграции.

**Ключевые слова:** ферроценовые катализаторы, скорость горения, твердое топливо, ферроценовые соединения, миграция.

Цитирование: Хабрат Г.Р. Методы предотвращения миграции катализатора ферроцена в твердое топливо / Г.Р. Хабрат, Ю.И. Пузин // Журн. Сиб. федер. ун-та. Техника и технологии, 2024, 17(7). С. 888–909. EDN: DCSUKH

### 1. Introduction

Solid fuels with high burning rates are one of the most important needs of the aerospace industry. One of the most common methods for producing such solid fuels is the use of needle catalysts. Catalysts or burn rate modifiers refer to a group of substances that increase or decrease the burning rate of propellants [1]. Another purpose of these compounds is to reduce the dependence of the combustion rate on temperature and pressure in the combustion chamber in order to create mesa and plateau regions on the time-thrust curve, which will improve the ballistic properties of the system [2]. An important and desirable feature of some compound engines is a low pressure profile and a high constant burning rate. According to studies, the use of intermediate metals significantly aggravates the oxidative destruction of polymers. For this reason, to produce solid fuels with high burning rates, it is necessary to use burning rate catalysts containing transition metals. It has been shown that an increase in the content of certain transition metals increases the combustion rate of fuel containing ammonium per chlorate (AP) [3, 4]. Transition metals serve as suitable substrates for catalytic processes, which increases the combustion rate. As a general classification, we can say: There are different types of burning rate catalysts (BRC) such as metal nanoparticles, intermediate metal oxides, metal chelates (organic metal chelates) and ferrocene-based polymers. Among the above catalysts, transition metal oxides are easily produced, available and low in price, but they are not able to significantly increase combustion rates, while organic metal chelates such as lead dimetal chelates are. And irons have good properties, including good dispensability and combustion enhancing properties. Ferrocene (Fc) catalysts are a typical example of BRC those required in lieu of very high burning rate in solid fuels, they are

considered the most widely used burning rate catalysts. In addition, they have uniform distribution (correct spreading) and good compatibility with organic binders compared to other compounds. It should be noted that the influence of the burning rate of ferrocene-based polymers depends on the chemical structure, solubility, molecular mobility and iron content [4]. In general, ballistic or catalytic modifiers are divided into two groups:

A) Oxides or salts of metals with different capacities of iron(II), acetylacetonate and metal chelates [5].

B) Liquid or solid organometallic compounds, such as ferrocene and its various derivatives, iron (II) acetylacetonate and metal chelates [5]. Ferrocene is an iron-related hydrocarbon derivative in which a ferrous ion (iron) is sandwiched between two cyclopentadienyl anions [6]. Ferrocene and its derivatives are widely used in various fields as catalysts, besides composites, pharmaceuticals, nanomaterials preparation and ion identification. Ferrocene is a volatile red solid that is used as a solid compound catalyst and has a higher burning rate than other metal compounds [7]. Since 1950, ferrocene and its derivatives have attracted much attention due to their high thermal stability, good electrochemical properties, and wide applications in chemical science and technology. Since 1960, these compounds have been used as combustion rate modifiers for solid fuels. Ferrocene has an electron-rich aromatic unit with electrochemical reversibility. Its derivatives also have the advantages of good variability, flammability and high molecular weight, as well as good thermal stability compared to other combustion catalysts [8]. Ferrocene-containing propellants undergo mechanical and ballistic changes during storage due to their volatility. For this reason, efforts are being made to find colored compounds and methods to prevent their evaporation [7].

The mechanism of operation of the catalysts is still not fully understood, which is due to the complexity of the mechanism of heat loss of ammonium perchlorate, since perchlorate contains four elements: nitrogen, hydrogen, chlorine and oxygen, as well as the study of the oxidation state of all four elements – this is almost out of 1000 possible chemical decomposition reactions. Forms ammonium perchlorate, but the mechanism of operation of these catalysts can be justified in four ways: A-Mechanism of electron transfer, B-Mechanism of proton transfer, C-Mechanism of formation of intermediate metallic substances, D-Interaction of acid and base. Due to the fact that ferrocene and the ferrocene cation is a suitable pair for the redox reaction, this reaction is closely related to the presence of the ferrocene ring. Electronic exchange is preferable to other mechanisms [9].

The influence of nickel oxide ( $\text{Ni}_2\text{O}_3$ ), iron oxide ( $\text{Fe}_2\text{O}_3$ ), manganese oxide ( $\text{MnO}_2$ ) and cobalt oxide ( $\text{Co}_2\text{O}_3$ ) on the decomposition reaction of ammonium perchlorate was studied and it was concluded that transition metal oxides can accelerate the decomposition of ammonium perchlorate. A possible mechanism for the formation of binuclear ferrocene compounds  $\text{Fe}_2\text{O}_3$  is shown in Figure (1). Heating binuclear compounds Fc first increases the distance between the rings of the cyclopentadienyl ligand and the iron atoms (Fc) under the attack of the oxygen atom AP, begins to decompose, and then cyclopentadienyl oxide rings and carbon dioxide are formed. Meanwhile, iron atoms and oxygen atoms quickly react to form tiny particles (nano-sized). These particles have a larger surface area than conventional powders.  $\text{Fe}_2\text{O}_3$  nanoparticles are excellent combustion rate catalysts and can accelerate thermal decomposition AP (Fig. 1) [10].

Among ferrocene derivatives, tert-butylferrocene (TBF), normal butylferrocene (NBF), and 2,2 – bis (ethylferrocenyl) propane (BEFP) or catocene are used as combustion rate catalysts in HTPB/

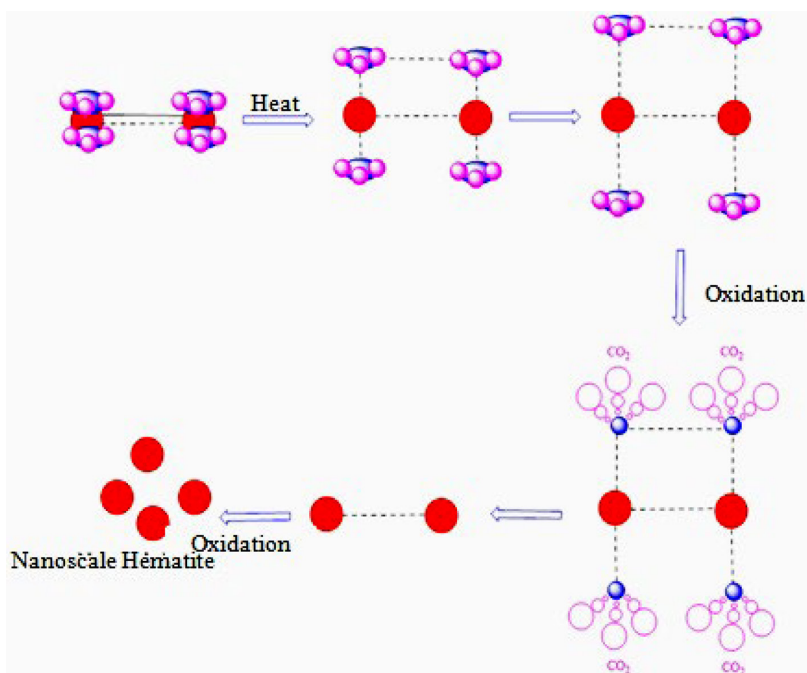


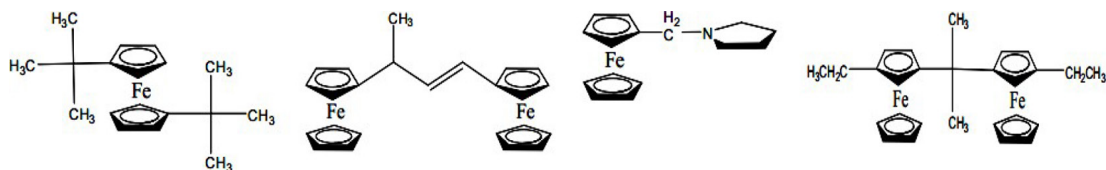
Fig. 1. Shows the possible mechanism of formation of nano Fe<sub>2</sub>O<sub>3</sub> from binuclear ferrocene molecule [4, 10, 11]

AP solid fuels [13]. Several disadvantages prevent their widespread use. For example, normal butyl ferrocene (NBF) migrates to the surface through the air, creating a layer around the engine that is prone to irritation from friction and impact [14].

Catocene is often added to fuels as a bridged dinuclear derivative of ferrocene to increase combustion rate [15]. This catalyst effectively increases combustion rate, reduces the pressure profile and provides good mechanical properties. Often its amount is less than 5 % by weight. The ratio of catocene to oxidizer can be more than 1 to 6. [16]. The mechanism of catocene formation during the thermal decomposition of AP as an oxidizer in mixed solid fuel can be studied by XPS [7].

Catocene, like some other ferrocene derivatives such as butacene, undergoes the phenomenon of migration, which causes disturbances in the performance of the engine. In addition to the issue of migration, the relatively high price of catocene and butacene is another obstacle for their use in the applications of composite propellants in the aerospace system [17]. The thermal decomposition effect of AP was investigated by differential thermal analysis (DTA) and thermal gravimetric analysis (TGA). The results of the work showed that the increase in the composition of ferrocene caused a decrease in the maximum temperature of decomposition of TM. Among the derivatives of ferrocene, catocene has a greater effect on the burning speed of [9].

Four ferrocene derivatives, including a 2,4-dinitrophenylhydrazine derivative with acetylferrocene, 1-pyrrolidinylmethylferrocene, di-tributylferrocene, and 1,3-diferrocenyl-1-butane (DFB) (Fig. 2), are based on ease of synthesis, high potency, and purity. Proposed for use in engines. The evaluation results showed that since DFB is liquid, it is easier to load as a solid; the compound also improves mechanical properties and increases combustion rates compared to conventional butylferrocene in compound and solid fuel-rich engines [18].



Di-tert-butyl ferrocene, 1,3-Diferrocenyl-1-butene, 1-Pyrrolidinyl Dimethyl ferrocene, Catocene

Fig. 2. The structure of several ferrocene derivatives [18]

In formulations made and cast with DFB, it has been observed that when toluene diisocyanate is used as a curing agent, it reduces the setting time of the propellant mixture and accelerates the curing process. In the comparison that was made in the same formulations with the combination of the following percentage and the presence of DFB and NBF catalysts (Table 1), the results showed that the effectiveness of DFB is similar to that of NBF. Also, comparing the presence of 1-pyrrolidinyl methyl ferrocene compound in the formulation increases the burning speed by 20 % compared to the presence of  $\text{Fe}_2\text{O}_3$  in the same formulation.

Also, this combination improves the tensile strength of TS, but the percentage of elongation decreases and also has no harmful effect during baking, so this combination is preferred over

$\text{Fe}_2\text{O}_3$ . Also tert-butyl ferrocene in propellant formulation improves the elongation percentage and in the presence of diisocyanate, accelerates curing and reduces its time [18].

Table 1. Comparison of burning speed and other characteristics of formulations containing ferrocene derivatives DFB and NBF

Formulation components (mass percentage)	Recipe № 1		Recipe № 2				Formulation 3		Formulation 4			
	A	Б	A	Б			A	Б	A	Б		
AP (250 $\mu$ ) (%)	33/5	33/5	8	8	23/5	33/5	33/5	33/5	8	8	23/5	33/5
AP (4 $\mu$ ) (%)	33/5	33/5	72	72	-	-	33/5	33/5	72	72	-	-
AP (810 $\mu$ ) (%)	-	-	-	-	33/5	33/5	-	-	-	-	33/5	33/5
binder	15	15	20	20	15	15	15	15	20	20	15	15
aluminum	17	17	-	-	17	17	17	17	-	-	17	17
NBF	2	-	2	-	-	-	2	-	2	-	-	-
DFB	-	2	-	2	-	-	-	2	-	2	-	-
Pyrrolidine methylferrocene	-	-	-	-	1	-	-	-	-	-	1	-
Di-tert-butyl ferrocene	-	-	-	-	-	1	-	-	-	-	-	1
Tensile strength (kg/c, m <sup>2</sup> )	7/5	8	7	7/2	12/6	10	7/5	8	7	7/2	12/6	10
Percentage of Length' increase	13	12	22	22	8	12	13	12	22	22	8	12
Burning speed (mm/s) in the 70 KSC	12/1	11/8	34	32	12	9/5	12/1	11/8	34	32	12	9/5

### 1.1. Nanocarbon derivatives

Adding carbon nano compounds to the ferrocene structure is another method of improving the combustion speed of the propellant [9]. Carbon is a very effective agent of redox reactions for  $\text{NO}_2$ ,  $\text{NO}$ ,  $\text{NO}$ ,  $\text{PbO}$  and other materials and can also change some propellant properties of  $\text{Pb-Cu-C}$  complexes not only for plateau (stabilization) or It affects the combustion process of the propellant, but it also causes a noticeable reduction in the pressure profile and improves the burning speed at low pressure. Carbon black, fluorescence, carbon fibers and carbon nanotubes (CNT) can be used in solid propellants; Carbon fibers can improve heat exchange and increase engine power and burning speed. Carbon fibers and carbon nanotubes in the engine increase the rate of decomposition of high-energy materials and increase the burning speed [19].

In this research, you prepared a complex containing ferrocene and  $\text{C}_{60}$  and the phenomenon of electron transfer between the electroactive group of electron donor and electron acceptor was investigated (Fig. 3) [9, 20].

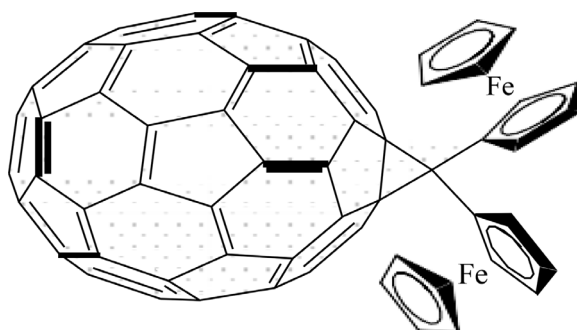


Fig. 3. Complex containing ferrocene and  $\text{C}_{60}$  [9]

### 1.1.2. Polymer derivatives

Some ferrocene-based polymers and its derivatives are widely considered as burning speed catalysts, especially for burning HTPB-based composite propellants. Of course, these polymers are also used as glucose sensors, protein and DNA sensors, immunosensors, carbon dioxide sensors, drug delivery nanocapsules, biosensors, etc [4, 21]. These compounds have been considered due to the good properties of ferrocenyl core compounds such as good thermal stability, evaporation and low migration [4].

## 2. Migration of ferrocene catalysts

As mentioned, ferrocene and its derivatives that contain alkyl, acyl and ester groups have a great effect on the burning speed of HTPB base propellants containing ammonium perchlorate and aluminum powders; But due to the fact that the short carbon chain has a low molecular weight, it evaporates easily during storage and the phenomenon of migration occurs, which takes the burning process of the propellant out of the desired state [22]. There are two possible mechanisms for migration:

A- Penetration mechanism; macroscopic migration and penetration of  $\text{Fc}$  derivatives into the next layers is due to the entropy increase process, which is also caused by the high concentration difference (Fig. 4).

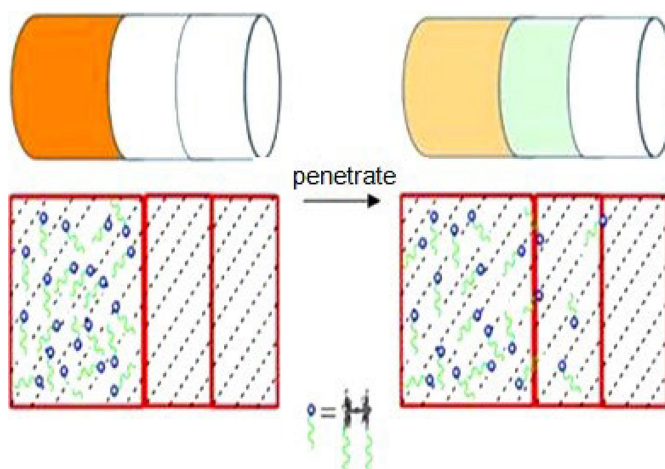


Fig. 4. Penetration of Fc derivatives in the engine [4, 10]

B- Mechanism of surface migration: the migration of Fc compounds from inside the engine to the interface and the formation of a coating in the intermediate phase; Catalyst small molecules act like surface active agents and migrate to the interface with the aim of reducing surface tension (Fig. 5) [4, 10].

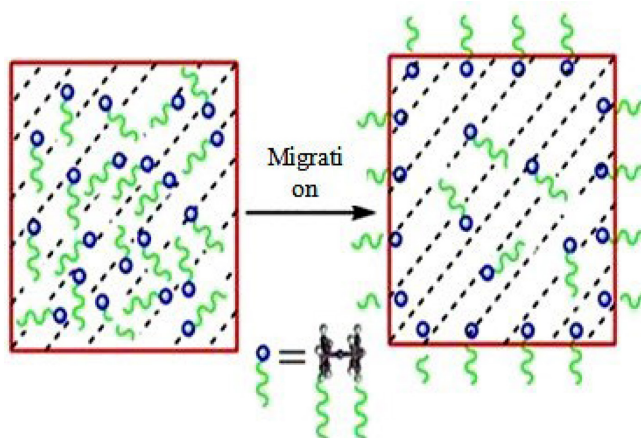


Fig. 5. Possible migration mechanism for Fc derivatives from the inside to the outside surface of the propellant [4, 10]

### 3. Methods of dealing with the migration of ferrocene derivatives

Many methods have been proposed to minimize or prevent the migration of ferrocene compounds. In general, there are two main theoretical solutions to improve the non-migratory property of Fc a) the method of increasing the alkyl chain to the ring, which increases the volume and weight by forming hyperbranched ferrocene compounds. b) The method of forming a network structure with cross-linking with two lights: the first method – adding active groups to ferrocenyl compounds to form a some

type network with cross-linking through the reaction with the curing agent (Fig. 6), which is due to the presence of ferrocenyl groups, such as They act as glue and prevent ferrocene evaporation so that ferrocene molecules can only move a little in the network.

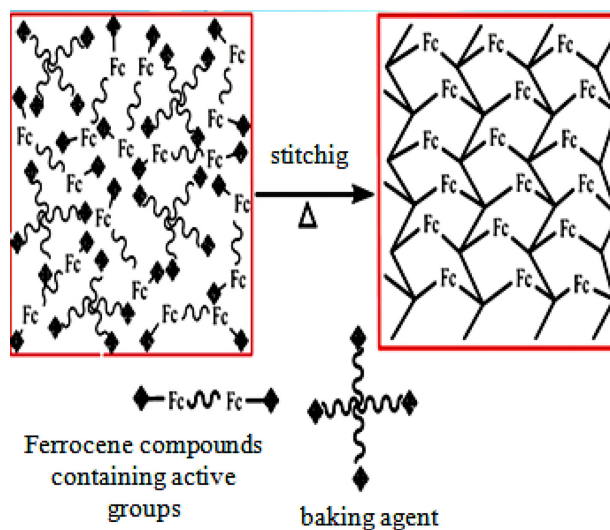


Fig. 6. The formation of a connected network containing ferrocene derivatives with Covalent bonds [4, 10]

The second method – increasing the cross-linking density to prevent Fc molecules from leaving the network and hindering the penetration and migration process (Fig. 7) [10]. These methods are described in detail below.

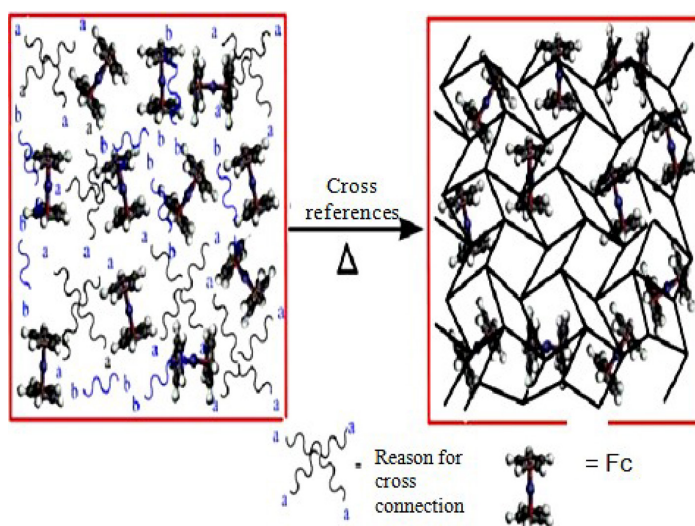


Fig. 7. Formation of a ferrocene cross-link network



### 3.1. Formation of hyperbranched ferrocene compounds (increase of alkyl chain to ring)

Hyper branching of polymers has attracted a lot of attention due to its unique features such as three-dimensional structure, low viscosity, high molecular weight, and suitable catalytic and electrical properties. Hyper branched polymers coated with ferrocene are large molecules with uniform distribution that have such characteristics [4].

Branching and connecting to a binder such as HTPB is one of the ways to prevent ferrocene migration in the propellant formulation. The cross-linking reaction for HTPB occurs by ferrocene-based epoxides, and after baking, the ferrocene unit becomes the fixed unit of the binder network; With this method, the amount of migration will be 8 to 10 times lower than normal [26]. For example, a schematic image of the migration of the system containing ferrocene without migration prevention methods is shown in Fig. 8. As can be seen, for the ferrocene sample, migration occurs easily in vacuum and at a temperature of 50 °C, while in the sample containing branched ferrocene (Fig. 9) in the same conditions, only a little displacement is seen and there is almost no migration [10].

It was suggested that the addition of ferrocenyl groups to HTPB or non-migratory polymers was done by the Friedel-Crafts reaction [13]. It has been observed that AP composite propellants based on HTPB/butacene binder having a low pressure profile value compared to other catalytic systems based on HTPB base, show a high burning rate so that it can be replaced by 50 % of HTPB with Boasen increased the burning rate [27]. In addition to having the above advantages for ferrocene grafted to polymers, these compounds also have disadvantages that have hindered their progress, including that ferrocenyl silane grafted to HTPB/butacene polymer, disadvantages such as the need for many steps, reaction dangerous, chlorination, Grignard reaction, etc.

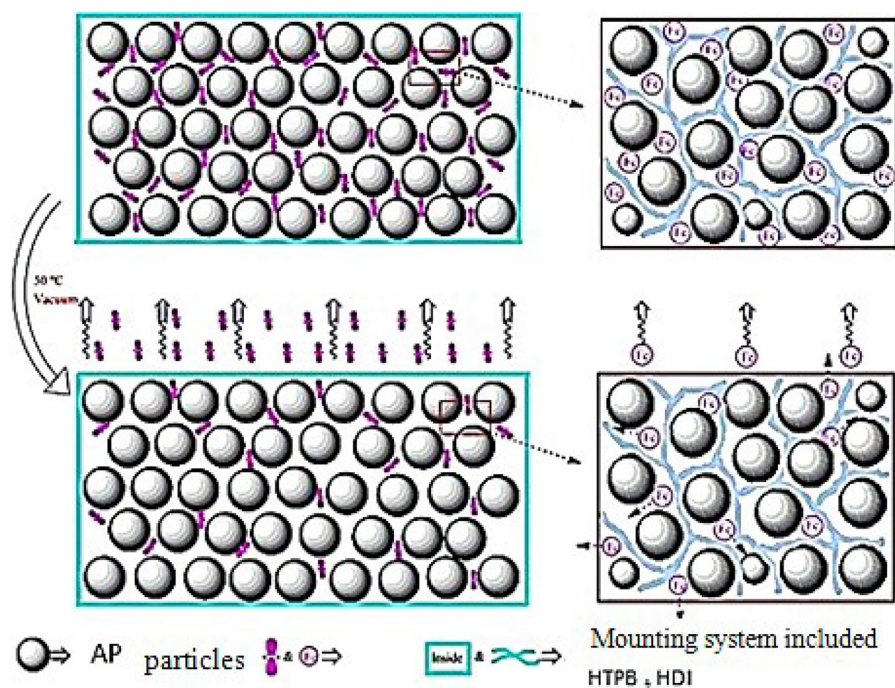


Fig. 8. An image of the migration phenomenon mechanism in the Fc/AP/HTPB/HDI system [10]

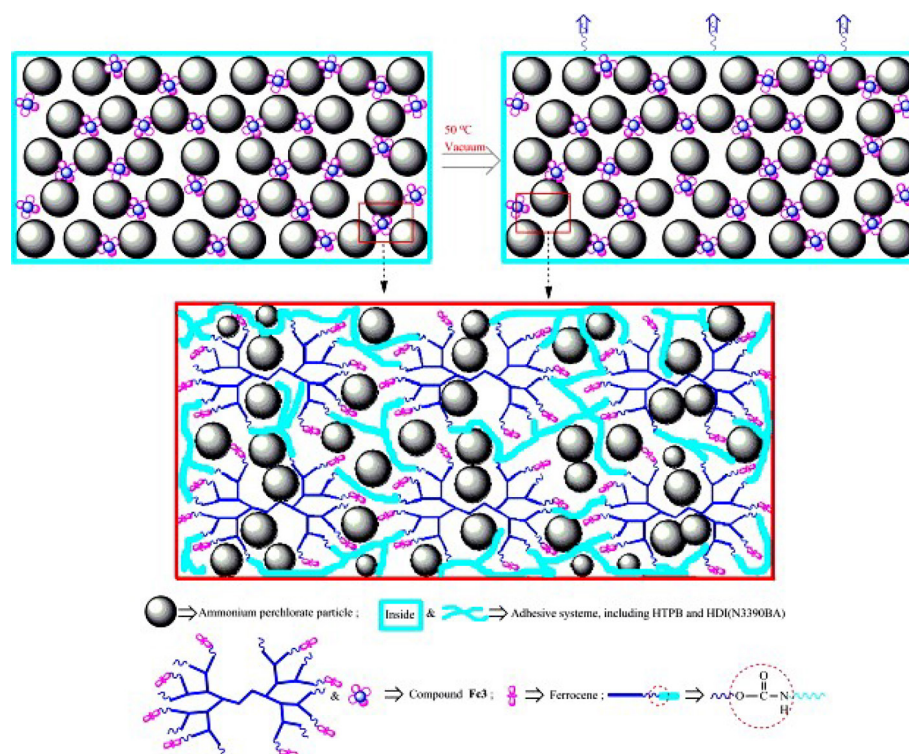


Fig. 9. Schematic of the anti migration mechanism in the Fe<sub>3</sub>/AP/HTPB/HDI system [10]

To overcome these disadvantages, four types of polyepichlorohydrin-2-methoxymethyloxirane (poly(ECH-co-MOMO)) samples were prepared by cationic ring-opening copolymerization method in the presence of  $-BF_3$  effects and 1,4-butane DL as the initiator. synthesized, modified ferrocene copolymers including ferrocene modified with (ECH-co-MOMO) as a burning rate catalyst are obtained from the reaction of ferrocene methanol with ECH in (ECH-co-MOMO) under alkaline conditions, from the results Investigations have revealed that the decomposition temperature of (ECH-co-MOMO) is higher than ferrocene modified with (ECH-co-MOMO) because the linear structure of (ECH-co-MOMO) has higher flexibility and chain mobility. provides, which leads to a decrease in  $T_g$ , while the dangling loop of modified ferrocene (ECH-co-MOMO) causes a limitation in the movement of the chain [28].

One of the other ways to deal with the migration of these catalysts is to use ferrocene containing multi-branched polyester polymers (HBPE-Fc). These compounds reduce migration due to the increase in molecular weight and the increase in intermolecular interaction through ferrocene bonding on the branched structure (HBPE-Fc) [26].

The results of the experiments have shown that (HBPE-Fc is much more stable than HBPE and the catalyst It is suitable for AP decomposition, so that the peak of low temperature heating (related to AP decomposition) after increasing 2 % by weight of G2 HBPE-Fc to AP from 328.8 °C (related to pure AP) to 6.201 °C and with an increase of 2 The weight% of G3 HBPE-Fc decreased to 188.3 °C with an increase of 2 weight% of G4 HBPE-Fc to 195.5 °C. It should be noted that the peak heat of ten high temperatures (related to the complete decomposition of AP) after these increases, it shifts from

427.3 °C (relative to pure AP) to about 290–330 °C. This large decrease indicates the catalytic effect of these compounds on the thermal decomposition of AP.

The structure of G2 HBPE-Fc with 12 ferrocenyl end groups is shown in Fig. 10. It is expected that with the increase of branches, the catalyst migration will decrease the burning rate. The G3-G4 HBPE-Fc structure is the same repeat of the G2 HBPE-Fc structure with 24 and 36 terminal ferrocene groups, respectively [29].

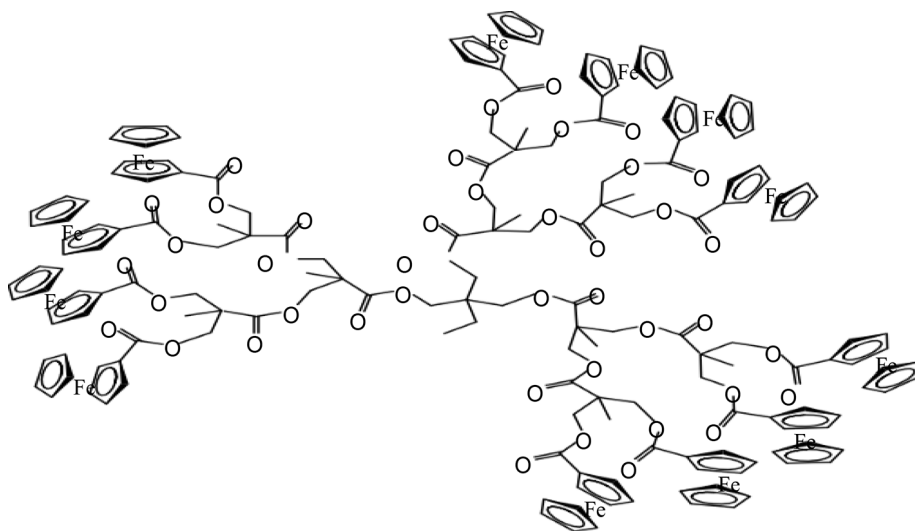


Fig. 10. Structure G2 HBPE-Fc [29]

Ferrocenes modified with hyperbranched polyamine esters (HPAE-Fc) are also used as combustion rate catalytic compounds [30–31]. The study showed that HPAE-Fc plays an effective role in the burning rate of AP-containing propellants. The migration characteristics were simulated at 60 °C, after 20 days, and at a distance of 14 mm from the interface (Fig. 11).

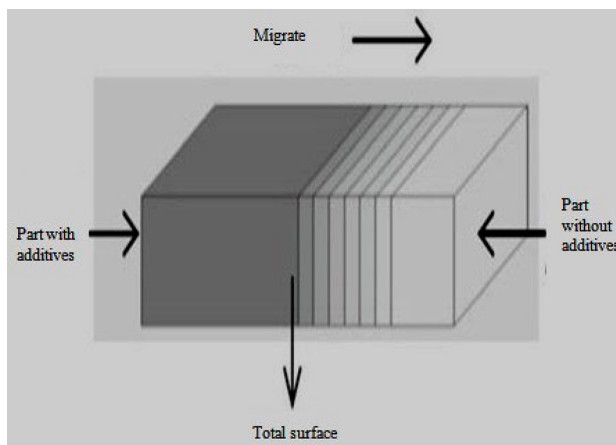


Fig. 11. Simulating the migration process of ferrocene compounds

The results showed that the migration concentration in the unloaded part is 0.14 mg/g for 38.1 mg/g, Fc G3-G4 HBPE- for carboxylic acid ferrocene and 36.4 mg/g for butyl ferrocene. Therefore, migration of Fc G3-G4 HBPE is ten times lower than carboxylic acid ferrocene and 30 times lower than butyl ferrocene. The structure of G2 HBPE-Fc with 12 and 24 end hydroxyl groups and G3 HPAE-Fc and G4 with 24 and 48 end ferrocene groups as well as tert-butyl ferrocene carboxylic acid ferrocene are shown in Fig. 12 [30].

The amount of migration and the migration penetration coefficient of HPAE-Fc are lower than carboxylic acid ferrocene and t-butyl ferrocene, so HPAE-Fc effectively reduces the migration of ferrocene in HTPB base elastomers. The catalytic mechanism can be described as the acceleration of radical formation by ferrocene components in HPAE-Fc and the separation of chemical bonds of gas molecules throughout the iron cluster catalyst [30]. For example, using HBPE-Fc reduces the activation energy of RDX decomposition and increases the rate constant of its thermal decomposition reaction. These catalytic changes may be related to the formation of a coordination bond between iron and N-NO in RDX due to the catalysis of iron clusters with a large surface area [26].

To measure the migration rate of HBPE-Fcs, ultraviolet absorption method can be used. In an experiment that was conducted to measure the migration between diethyl ferrocene and tertibutyl

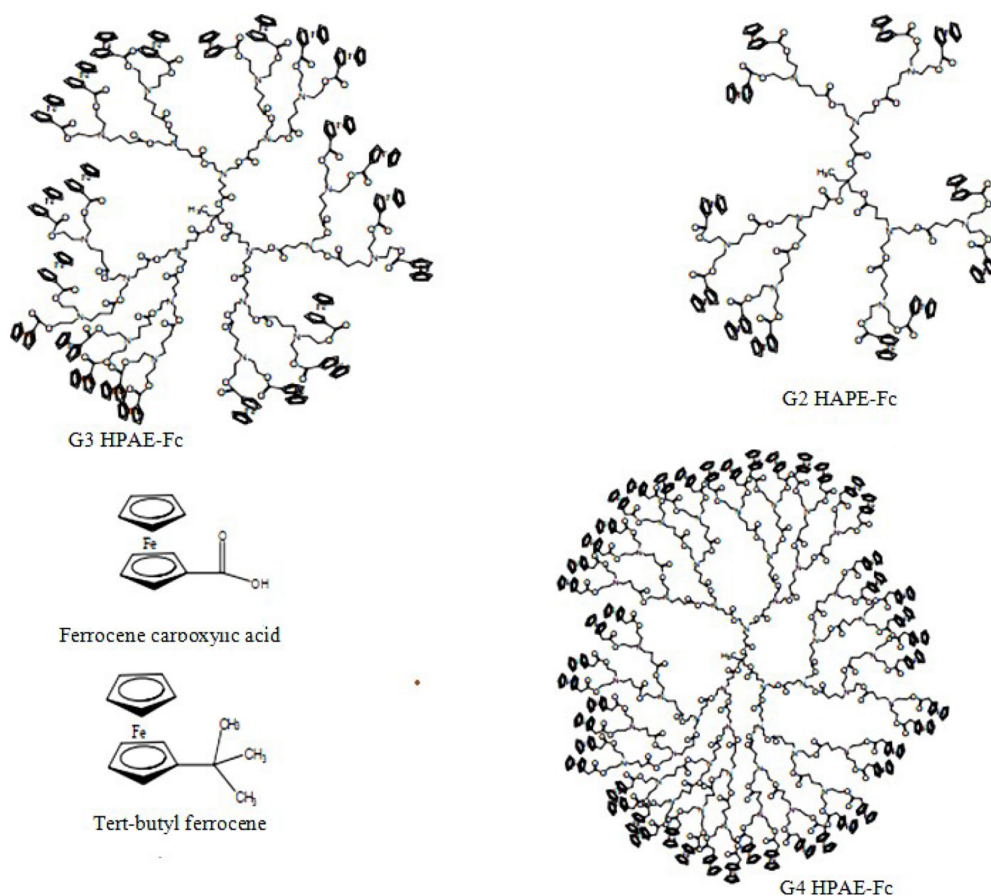


Fig. 12. Structure of carboxylic acid ferrocene and tetra-butyl ferrocene and G2-G3 HPAE with 12 and 24 terminal hydroxyl groups and G2-G4 HPAE-Fc with 12, 24 and 48 terminal ferrocene groups [30]

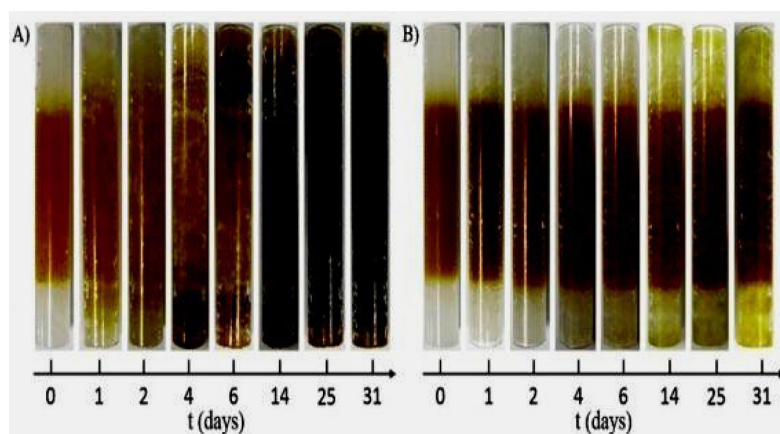


Fig. 13. Images of A) ferrocene migration tube and B) migration of HBPE-g-PFcEMA after different times at 50 °C [32]

ferrocene and compare it with HBPE-Fcs, it was shown that the amount of migration in HBPE-Fcs is lower than the other two compounds (Fig. 13). However, ferrocene bonded with different side groups shows different UV/Vis absorption capabilities [26] and the diffusion coefficient of HBPE-Fcs is noticeably lower than diethyl ferrocene and tert-butyl ferrocene. Observations predict that HBPE-Fcs can effectively reduce migration in HBPEs elastomer (Fig.14).

Another branched ferrocene compound used to reduce migration is hyperbranched ferrocene with polyethylene (HBPE-g-PFcEMA). The thermal stability of this compound was evaluated using the TGA technique and its decomposition temperature was reported to be around 210 degrees Celsius. By comparing two samples A (without polyethylene branching) and sample B (with (HBPE-g-PFcEMA), it was shown that for sample A, the migration started from the first day and the migration of ferrocene

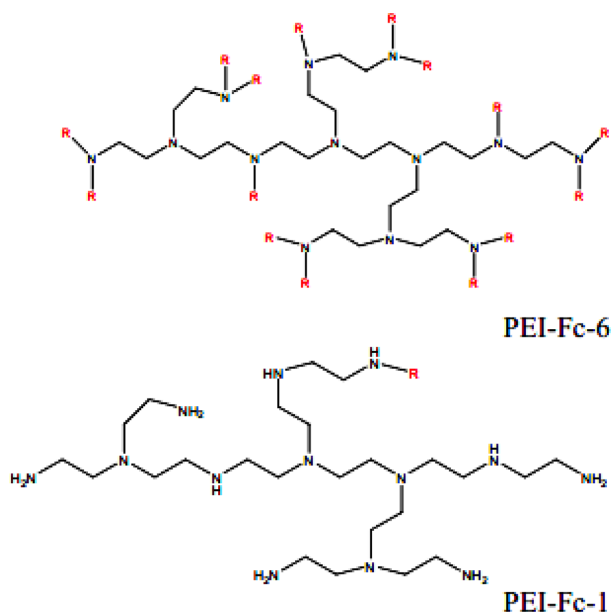


Fig. 14. PEI-Fcs and R=Fc derivatives [11]

after 6 days of storage in it The temperature of 50 °C has intensified, while the HBPE-g-PFcEMA composite has shown good anti-migration properties, even after 31 days, a little migration (HBPE-g-PFcEMA) is observed, so it can be concluded (HBPE-g-PFcEMA is one of the most effective burning rate catalysts with low migration [32].

In another study, ferrocenes based on polyethyleneimines (PEI-Fcs) have been used as catalysts for burning speed with low migration, six types of derivatives of PEI-Fcs have been synthesized and investigated by substituting amino hydrogen. (Fig. 14) [11].

These compounds are thermally stable. TG and DTG studies for PEI-Fcs have shown high catalytic activity to reduce the thermal decomposition temperature of AP (11)

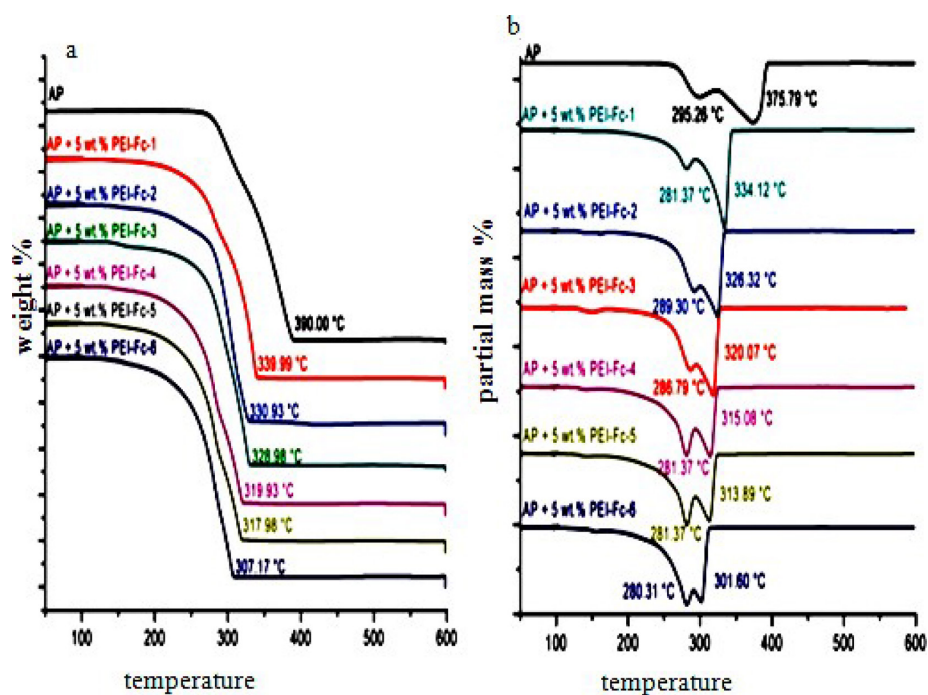


Fig. 15. TG curve for pure AP and 5 % by weight PEI-Fcs (a) and DTG curve for pure AP and 5 % by weight PEI-Fcs (b) [11]

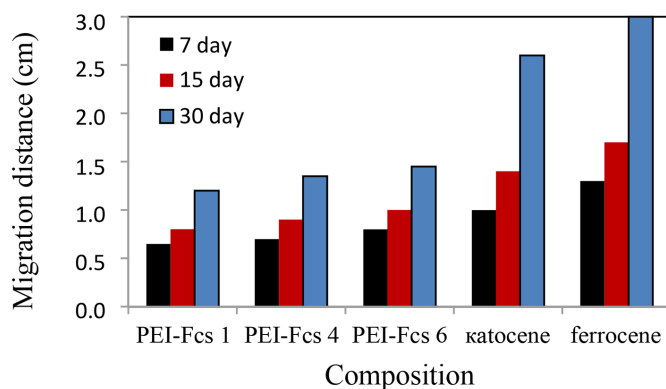


Fig. 16. Migration study of PEI-Fcs-6, PEI-Fcs-4, PEI-Fcs-I, katocene and ferrocene at 50 °C

The migration of several PEI-Fcs derivatives with catocene and ferrocene was studied using the sample tube method (Fig. 16). Based on the studies carried out with these compounds, it can be concluded that the new low migration PEI-Fcs have the potential to reduce the thermal decomposition temperature of AP [11].

### *3.2. Increase of active groups to ferrocenyl compounds*

#### *3.2.1. Combining ferrocene with polar groups and forming a complex*

Designing ferrocene groups containing polar groups such as azolyl, hydroxyl (such as bisferrocenyl hydroxyl), acyl groups or complex derivatives of transition metals with ferrocene base ligands that tend to form hydrogen bonds or  $\pi$ - $\pi$  is another method. Prevention of migration is age-old. In this investigation, hydroxyl bisferrocenyl propane was prepared and its effect was investigated as the burning rate and it was observed that the burning rate increases by 1.5 % [9]. Also, the comparison of the catalyst with other ferrocene derivatives showed that it has a lower heat transfer rate than tert-butyl ferrocene (TBF). A new derivative of ferrocene, including 1, 1-bis-(trimethylsiloxane ethyl) ferrocene (BTEF), was synthesized and the results showed that it is effective in improving the burning speed, mechanical properties and process of AP/HTPB propellants. Synthesis of cyclostyle ferrocene base, 1,6-bicyclooctyl ferrocene base and 1,3-bicyclooctyl ferrocene base by Friedel-Crafts reaction in the presence of Fc and z- cyclooctene or cyclohexene with  $AlCl_3$  as an acid catalyst. Lewis, the research results showed that cycloalkyl-based ferrocene derivatives have a high potential for use in AP/HTPB-based solid propellants. Nitrogenous heterocyclic polynuclear ferrocene derivatives (NHPNFD) have also been synthesized using ferrocene-bound formylpropyl and ferrocene-bound acetylpropyl. The results of DSC and TG analyzes have shown that NHPNFD can improve the thermal decomposition performance of AP as soon as it increases by 5 % by weight [33].

#### *3.3. Creation of ionic bonds using ionic liquids and polycyano*

Energetic ionic compounds are considered a competitor to other similar non-ionic aromatic compounds due to their low vapor pressure, higher density, high heat of formation, high thermal stability, better oxygen balance and compatibility with the environment. Some Bonny compounds derived from decanuclear ferrocene have been synthesized and investigated. All the derivatives of these compounds have shown high thermal stability and low migration speed compared to Catocene. These compounds have high catalytic activity in thermal decomposition of AP and RDX. Derivative N, N'-bis(ferrocenylmethyl)-dimethyl 1,3-propylene diammonium dinitrate (Fig. 17) is one of these derivatives that has shown the best catalytic effect in the thermal decomposition of AP and can be a suitable option as a catalyst for the burning rate of ferrocene base in HTPB/AP composite propellant [34].

The design and synthesis of a series of ferrocene-based mono- and dinuclear ionic compounds with nitrate or picrate as counter anions have been considered to prepare burning rate catalysts with low or no migration. In a research, ferrocenyl methyl alkyl imidazolium (triazolium) iodide was selected as a cationic source of new energetic ionic compounds [12]. The selected source of cation contains a nitrogen-rich heterocyclic ring, which contributes to their thermal stability and migration characteristics and the level of energy generation of propellants, and also the important point about these materials is their easy preparation. 1- Ferrocenyl methylimidazolium (triazolium) with PF6 –

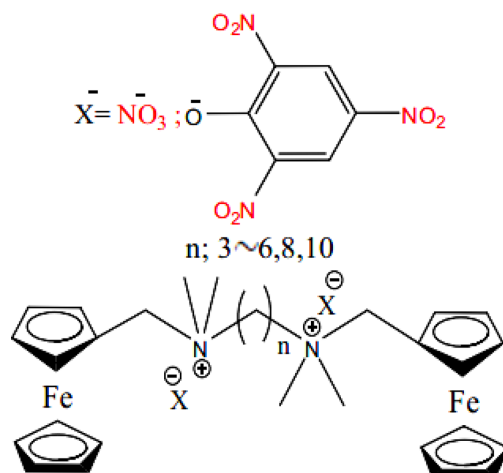


Fig. 17. Molecular structure of N, N'-bis(ferrocenylmethyl) dimethylalkynyl diammonium dinitrate and dipicrate (alkyl chain length  $n=3-6,8,10$ )

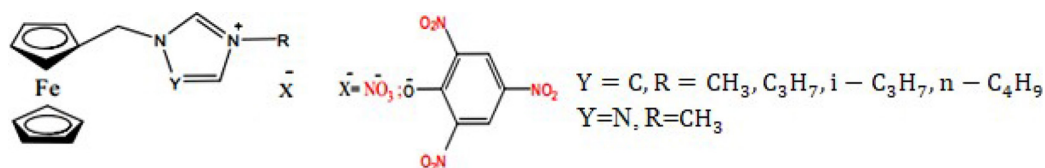


Fig. 18. Molecular structure of 1-ferrocenylmethyl d-(4)-alkyl imidazolium (triazolium) nitrate and picrate [12]

or NTF<sup>-</sup> (NTF<sub>2</sub>) or bistrifluoromethanesulfonylamide) to exchange iodides as the counter ion of these compounds has been prepared and some of them are ionic liquids [12].

In another experiment to prepare energetic ferrocene ionic compounds, ferrocenylmethylalkyl imidazolium (triazolium) iodides have been selected as cation sources. The selected cationic sources contain nitrogen-rich heterocyclic rings that provide high thermal stability, low migration characteristics, and energy generation for propellants, and most importantly, their easy preparation, which are the main advantages of these compounds. The combination of 1-ferrocenylmethyl-3-(4)alkylimidazolium (triazolium) nitrate and picrate has been designed and synthesized for this purpose. In a study, twelve new compounds of ferrocenyl methylimidazole triazole based on nitrate and picrate were prepared; all of these compounds are thermally stable and have very low ion migration. These compounds are: [12].

1-Ferrocenylmethyl-3-methylimidazolium nitrate	1-Ferrocenyl methyl-3-methylimidazolium picrate
1-Ferrocenylmethyl-3-ethylimidazolium nitrate	1-Ferrocenyl methyl-3-ethylimidazolium picrate
1-Ferrocenylmethyl-3-propylimidazolium nitrate	1-Ferrocenylmethyl-3-propylimidazolium picrate
1-Ferrocenylmethyl-3-isopropylimidazolium nitrate (aqueous)	Isopropylimidazolium picrate
1-Ferrocenylmethyl-3-butylimidazolium nitrate	1-Ferrocenyl methyl-3-butylimidazolium picrate
1-Ferrocenylmethyl-3-methyltriazolium nitrate (1/2 water)	1-Ferrocenyl methyl-3-methyltriazolium picrate



These compounds have high catalytic activity for thermal decomposition of AP and two compounds containing triazole ring have more activity than imidazole ring. However, their catalytic activity has been reported to be less than ferrocene binuclear compounds. It should be noted that the design and synthesis of nitrogen-rich polynuclear heterocyclic ring compounds, such as triazole and tetrazole, are still part of the research programs

Polycyano anions as nitrogen-rich anions are proposed as counterions for high-energy nitrogen-rich ionic materials, and their resulting salts show higher standard enthalpies of formation than their nitrate analogs. Polycyano anions are used in the field of ionic liquids and crystal engineering and have a high level of electron destabilization. Three types of polycyano anions have been selected as anions to pair with 1-ferrocenylmethyl-3-alkylimidazolium cations and form new ionic ferrocene compounds (Fig. 19) (13), which include 1:1, 1, 3, 3-tetracyanopropenide (TCP), compound 1, 1, 2, 3, 3-pentacyanopropenide (PCP) and compound 1, 1, 2, 5, 6, 6- hexacyano-3-4 – They are diaza hexa dianide (HCP)<sup>3</sup>

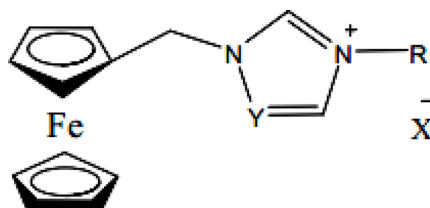
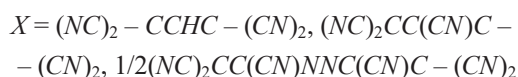
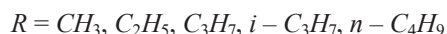


Fig. 19. Molecular structure of 1-ferrocenylmethyl-3-alkylimidazolium bound to polycyanobase anions [13]

Research results in this area have shown that polycyano-based ionic ferrocenyl compounds are among the best proposals for improving the anti-migration properties of ferrocene-based needle catalysts. The migration of ionic compounds is significantly lower than that of Catocene. Polycyanobasic compounds exhibit high catalytic activity during the thermal decomposition of AP and exceed the corresponding nitrates and picrates. These compounds have also demonstrated their catalytic effect in many compounds such as RDX, but the thermal decomposition of HMX has not been reported. (13.6) the tendency to migrate of four polycyano- based compounds: 1 ferrocenylmethyl-3-propylimidazolium, 1,1,2,3,3-pentacyanopropenide (compound B), bis(1-ferrocenylmethyl-3-propylimidazolium) 1, 1, 2, 6, 6-hexacyano-3, 4-diazahexadiazide (compound C) with catosine and compound A-B-C during 7 days of aging, respectively  $\pm 32.86$  were 1.95 %,  $3.26 \pm 0.13$  %,  $2.68 \pm 0.15$  % and  $0.95 \pm 0.06$  %, respectively. reported. The graph also shows the willingness to migrate within 14 and 30 days of senescence. The degree of migration reduction for the mentioned compounds was assessed as  $A > C > B$ , and it was found that increasing the molecular weight of the compound reduced the degree of migration.

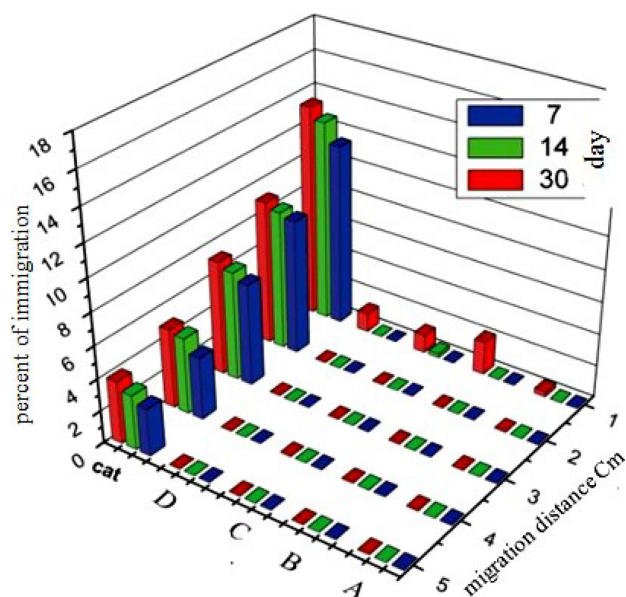


Fig. 20. The relationship between the migration percentage of compound A, B, C and Catocene (Kat) on migration distance and aging time at 70 °C

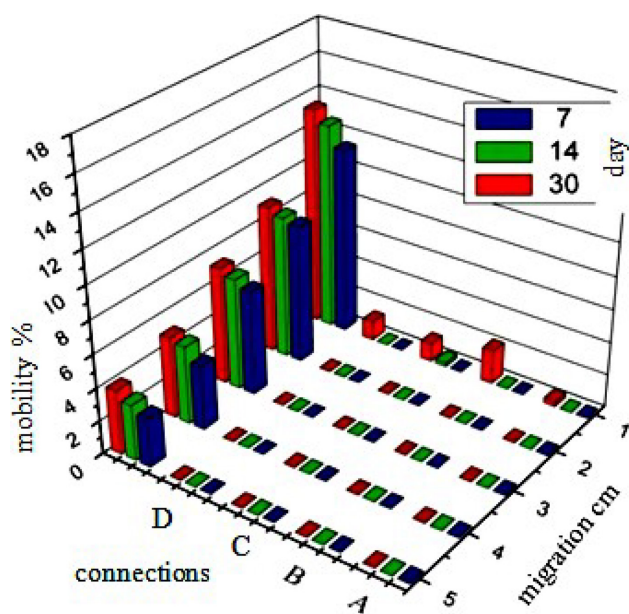


Fig. 21. Tendency to migrate for compounds A, B, C, D and Catocene along with migration distance and different aging times (at 70 °C temperature) [35]

In recent years, a number of ferrocenyl ionic compounds based on on 5-ferrocenyl-1H-tetrazole (HFcTz) have been designed and synthesized, and their migration is lower compared to catocene. In addition to having a fersane group, this compound is also rich in nitrogen and can be easily deprotonated to form an anion rich in ferrocenyl nitrogen. Based on this, relative mobility for four compounds guadinium 5-ferrocenyl-H-tetrazolate (compound B), 1-octyl-3- methylimidazolium-5-ferrocenyl-1 1H-tetrazolate (compound C) and 1-dodecyl-3- methylimidazolium- 5-ferrocenyl-1H-

tetrazolate (compound D) and catocene in connection with HTPB migration distance and aging time are shown in Fig. 21 [35].

It is clearly seen that the amount of migration of ionic compounds is significantly less than that of Catocene. The tested compounds are not very detectable after 7 to 15 days, but after 30 days of their life (aging) at 70 degrees Celsius, the amount of total migration for the new compounds, it is 30, 1.17, 1.10 and 2.07 %, respectively, while the migration ratio for Catosen on the 30th day under the same conditions is calculated as 32.86 %. That the lowest migration for compound 1 was evaluated to be due to hydrogen-rich bonding interactions.

### Conclusion

Considering the necessity of the presence of burning speed catalysts in the formulation of solid propellants and also having conditions such as easy access, low price and ease of use, non-migration of ferrocene compounds are among the famous catalysts in this field. But the existence of the problem of migration over time and creating the risk of storing engines containing these burning speed catalysts has doubled the need for measures to prevent this process. According to what was stated in the above sections, there are several main methods to prevent migration: a) increasing the chain to ferrocene b) adding the network with curing agents and other formulation components c) using ionic liquids in the chain addition method. Ferrocene can act both as a main component and as a pendant chain. In the network method, hyperbranched ferrocene compounds are formed in combination with a binder such as HTPB or amino polyesters, which nitrogen-rich amino compounds also compensate for energy loss. The method of using ionic liquids is another method. It is due to the easy combination of components, the energy-generating nature of most of these tribots, as well as the wide range of ionic liquid groups considered by researchers in the field of propulsion. Considering that the amount of energy generation, easy preparation method, lifetime, the amount of influence on increasing the combustion speed of the propellant, and the amount of migration are effective in choosing the catalyst for the burning speed, and according to the contents mentioned in the article, branched ferrocenes can be used. introduced as one of the best burning speed catalyst with low and effective migration. Considering the wide range of materials that can be combined with ferrocene, as well as the variety of methods, and taking into account the priorities of the propellant manufacturing industries, such as ease of manufacturing, excess material abundance, high efficiency, process safety, etc., there is a need for extensive studies in the field of catalysts. The burning speed of the ferrosen base can be done.

### References

- [1] Sutton G.P., Biblarz O. Rocket Propulsion Elements. Wiley, 2016.
- [2] Abdin Z. U., Yu H., Wang L., Saleem M., Khalid H., Abbasi N.M. & Akram M. Synthesis, anti-migration and burning rate catalytic mechanism of ferrocene-based compounds. *Applied Organometallic Chemistry*, 2014, 28(8), 567–575. DOI: 10.1002/aoc.3166.
- [3] Sharma J.K., Srivastava P. & Singh G. Nanocatalysts: Potential burning rate modifier for composite solid propellants. *Materials Focus*, 2014, 3(2), 81–91. DOI: org/10.1166/mat.2014.1154
- [4] Gao X., Li J., Luo Y., Li C., Bi F., Zhang W. & Gao Z. Ionic ferrocenyl compounds containing polycyano anions. Synthesis, structures, and effects on thermal decomposition of core components of

solid propellants. *Zeitschrift für anorganische und allgemeine Chemie*, 2015, 641(2), 475–482. DOI: 10.1002/zaac.201400467

[5] Jiang B., Zhang W., Yang J., Yu Y., Bao T. & Zhou X. Low-Temperature Oxidation of Catocene and Its Influence on the Mechanical Sensitivities of a Fine-AP/Catocene Mixture. *Propellants, Explosives, Pyrotechnics*, 2015, 40(6), 854–859. DOI: 10.1002/prop.201500099

[6] Zhuo J. B., Li H.D., Lin C.X., Xie L.L., Bai S. & Yuan Y.F. Ferrocene-based sulfonyl dihydropyrazole derivatives: Synthesis, structure, electrochemistry and effect on thermal decomposition of NH<sub>4</sub>ClO<sub>4</sub>. *Journal of Molecular Structure*, 2014, 1067, 112–119.

[7] Zhuo J. B., Li H.D., Lin C.X., Xie L.L., Bai S. & Yuan Y.F. Ferrocene-based sulfonyl dihydropyrazole derivatives: Synthesis, structure, electrochemistry and effect on thermal decomposition of NH<sub>4</sub>ClO<sub>4</sub>. *Journal of Molecular Structure*, 2014, 1067, 112–119.

[8] Tong R., Zhao Y., Wang L., Yu H., Ren F., Saleem M. & Amer W. A. Recent research progress in the synthesis and properties of burning rate catalysts based on ferrocene- containing polymers and derivatives. *Journal of Organometallic Chemistry*, 2014, 755, 16–32.

[9] Wang L., Yu H., Saleem M., Akram M., Abbasi N. M., Khalid H. & Chen Y. Ferrocene-based polyethylene imines for burning rate catalysts. *New Journal of Chemistry*, 2016, 40(4), 3155–3163. DOI: 10.1039/x0xx00000x

[10] Liu X., Zhang W., Zhang G. & Gao Z. Low-migratory ionic ferrocene-based burning rate catalysts with high combustion catalytic efficiency. *New Journal of Chemistry*, 2015, 39(1), 155–162. DOI: 10.1039/C4NJ01216J

[11] Liu X., Li J., Bi F., Zhang W., Zhang G. & Gao Z. Ionic Ferrocene-Based Burning-Rate Catalysts with Polycyano Anions: Synthesis, Structural Characterization, Migration, and Catalytic Effects during Combustion. *European Journal of Inorganic Chemistry*, 2015 (9), 1496–1504. DOI:10.1002/ejic.201403023

[12] Gore G. M., Bhatewara R. G., Tipare K. R., Nazare A. N. & Asthana S. N. Studies on Ferrocene PolyGlycol Oligomer – Burning Rate Modifier for Composite Propellants. *Journal of propulsion and power*, 2004, 20(4), 758–760. doi.org/10.2514/1.11460

[13] Gao Y., Li H.D., Ke C. F., Xie L. L., Wei B. & Yuan Y. F. Synthesis of dihydropyrazole-bridged dinuclear ferrocenyl derivatives and their catalytic effect on thermal decomposition of ammonium perchlorate. *Applied Organometallic Chemistry*, 2011, 25(6), 407–411. DOI 10.1002/aoc.1774

[14] Liu L. L., He G. Q., Wang Y. H. & Liu P. J. Effect of catocene on the thermal decomposition of ammonium perchlorate and octogen. *Journal of Thermal Analysis and Calorimetry*, 2014, 117, 621–628. DOI 10.1007/s10973–014–3792–5

[15] Çikalın S. A. «Synthesis of Ferrocenyl Quinones and Ferrocenyl Based Burning Rate Catalysts.» M. S. Thesis Chemistry, The Middle East Technical University, 2003.

[16] Gore G. M., Tipare K. R., Bhatewara R. G., Prasad U. S., Gupta, M. & Mane S. K. Evaluation of ferrocene derivatives as burn rate modifiers in AP/HTPB-based composite propellants. *Defence Science Journal*, 1999, 49(2), 151–158

[17] Kay K. Y., Kim L. H. & Oh I. C. The first methano-bridged diferrocenyl fullerene (C 60). *Tetrahedron Letters*, 2000, 41(9), 1397–1400.

[18] Wang H., Zhao F. Q., Li S. W. & Gao H. Function of carbon materials used in solid propellants and their action mechanism. *Chinese Journal of Explosives and Propellants*, 2006, 29(4), 32. doi:10.1088/1742–6596/2021/1/012018

- [19] Takahashi S. & Anzai J.I. Recent progress in ferrocene-modified thin films and nanoparticles for biosensors. *Materials*, 2013, 6(12), 5742–5762. doi.org/10.3390/ma6125742
- [20] Vuga S.M. Effects of liquid burn rate catalysts on Rheological Properties of High-Energy Composite Propellants. *Propellants, explosives, pyrotechnics*, 1991, 16(6), 293–298. doi.org/10.1002/prop.19910160607
- [21] Nguyen T.T. The effects of ferrocenic and carborane derivative burn rate catalysts in AP composite propellant combustion: mechanism of ferrocene-catalysed combustion. DSTO Aeronautical and Maritime Research Laboratory. 1995, 39
- [22] Nguyen T.T. New Insights into the Combustion of AP/HTPB Rocket Propellants: The Catalyst Active Sites and a Combustion Flame Model for The Ferrocene-Catalysed Combustion. *International Journal of Energetic Materials and Chemical Propulsion*, 1997, 4(1–6). DOI: 10.1615/IntJEnergeticMaterialsChemProp.v4.i1–6.640
- [23] Xiao F., Feng F., Li L. & Zhang D. Investigation on ultraviolet absorption properties, migration, and catalytic performances of ferrocene-modified hyper-branched polyesters. *Propellants, Explosives, Pyrotechnics*, 2013, 38(3), 358–365. DOI: 10.1002/prop.201200126
- [24] Ghosh K., Behera S., Kumar A., Padale B.G., Deshpande D.G., Kumar A. & Gupta M. Studies on Aluminized, high burning rate, Butacene® based, composite propellants. *Central European Journal of Energetic Materials*, 2014, 11(3), 323–333.
- [25] Cho B. S. & Noh S.T. Synthesis and thermal properties of ferrocene-modified poly (epichlorohydrin-co-2-(methoxymethyl) oxirane). *Macromolecular Research*, 2013, 21, 221–227. DOI 10.1007/s13233–013–1074-x.
- [26] Xiao F. J. & Luo Y.J. Ferrocene containing hyperbranched polyester: Structure and catalytic performance for thermal decomposition of ammonium perchlorate. *Advanced Materials Research*, 2011, 197, 1225–1230. doi.org/10.4028/www.scientific.
- [27] Xiao F., Yu X., Feng F., Sun X., Wu X. & Luo Y. Investigation of the redox property, migration and catalytic performance of ferrocene-modified hyperbranched poly (amine) ester. *Journal of Inorganic and Organometallic Polymers and Materials*, 2013, 23, 315–324. DOI 10.1007/s10904–012–9778–5
- [28] Fengjuan X., Minmei S., Lei P., Yunjun L. & Junchai Z. Ferrocene end-cap hyperbranched poly (amine-ester): structure and catalytic performance for thermal decomposition of ammonium perchlorate. *Journal of Inorganic and Organometallic Polymers and Materials*, 2011, 21, 175–181. DOI 10.1007/s10904–010–9428–8
- [29] Amin B. U., Yu H., Wang L., Fahad S., Nazir A., Haq F. & Liang R. Synthesis and anti-migration studies of ferrocene-based amides as burning rate catalysts. *Journal of Inorganic and Organometallic Polymers and Materials*, 2021, 31, 2511–2520. doi.org/10.1007/s10904–020–01861–7
- [30] Zhao H., Guo L., Chen S. & Bian Z. Synthesis, complexation of 1, 2, 3-(NH)- triazolylferrocene derivatives and their catalytic effect on thermal decomposition of ammonium perchlorate. *RSC advances*, 2013, 3(43), 19929–19932. doi.org/10.1039/C3RA43117G
- [31] Gao Y., Li H., Ke C., Xie L. & Yuan Y. Design and synthesis of combustion catalysts bearing nitrogenous heterocyclic polynuclear ferrocenyl derivatives. *Chem Propellants Polym Mater*, 2010, 8, 34–7. doi.org/10.1080/10406638.2023.2167215
- [32] Lai Zheng-Mao, Hong-Min Ye, Qian Wan, Li-Li Xie, Sha Bai and Yao-Feng Yuan. «Synthesis, crystal structure and properties of benzimidazole-bridged dinuclear ferrocenyl derivatives.» *Journal of Molecular Structure*, 2014, 1059, 33–39.

[33] Gao Y., Li H. D., Ke C. F., Xie L. L., Wei B. & Yuan Y. F. Synthesis of dihydropyrazole-bridged dinuclear ferrocenyl derivatives and their catalytic effect on thermal decomposition of ammonium perchlorate. *Applied Organometallic Chemistry*, 2011, 25(6), 407–411. DOI 10.1002/aoc.1774.

[34] Cheng Z., Zhang G., Fan X., Bi F., Zhao F., Zhang W. & Gao Z. Synthesis, characterization, migration and catalytic effects of energetic ionic ferrocene compounds on thermal decomposition of main components of solid propellants. *Inorganica Chimica Acta*, 2014, 421, 191–199.

[35] Pavase T. R., Lin H., Hussain S., Li Z., Ahmed I., Lv L. & Kalhor M. T. Recent advances of conjugated polymer (CP) nanocomposite-based chemical sensors and their applications in food spoilage detection: A comprehensive review. *Sensors and Actuators B: Chemical*, 2018, 273, 1113–1138