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The Effect of Additives on Solid Rocket Propellant Characteristics

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The effect of different additives on viscosity gradient of composite rocket propellants (CRP) based on hydroxytermi-nated polybutadiene (HTPB) cured with isophorone-diisocyanate (IPDI) or dimeryl-diisocyanate (DDI) containing ferry-oxide or copper- chromite and CRP based on polyurethane (PU), cured with toluene-diisocyanate containing ferry-oxide are presented in this paper.
The effect of tetracycline (TC), pyrogallol (PG), diester of phosphoric acid (RM-410), acetylacetone (HAA) and curing catalyst comprising triphenyl bismuth (TFBi), maleic anhydride (MA) and magnesium oxide (MgO) on propellant viscosity and cure rate profile is also given.

Key words: **composite rocket propellant, viscosity, additives, effect of additives, additive effect tetracycline, pyrogallol, triphenyl bismuth, acetyl acetone.**

Introduction

APART from the basic components, such as oxidizer, mostly ammonium perchlorate (AP) and binder, as cured polymer containing plasticizer, bonding agent, antioksidant, curing rate modifier etc. which regulate physico-chemical and mechanical characteristics, composite rocket propellants (CRP) comprise versatile additives. Some of them function as burning rate modifiers, mechanical characteristic additives, improve processibility etc. The physico-chemical behaviour of propellants vary significantly depending on the additive type and quantity. In addition to the effect of the catalyst on polymer curing, these compounds can establish the secondary bonding to propellant components and influence the viscosity and mechanical characteristics of the CRP.

During many grains production processes from CRP as thermosetting material hardening at enhanced temperature, propellant viscosity is required. The minimum time needed within which the propellant cast is satisfactory must be observed, so that homogeneous propellant consistency is provided during grain casting. If viscosity value changes significantly over time, quality of the grain can vary depending on the period of the casting process: has it been cast at the beginning or end of the process.

The available time for homogenizing and casting the propellant after adding the curing agent is called "pot life" in the terminology of CRP. That period depends on the curing system, type and quantity of the filler and additives present. In most cases, a small amount of burning rate catalyst, especially iron, chrome and copper compounds, shorten the pot life [1, 2]. In order to prevent such effect, additives with which metals from these catalysts build appropriate, non-catalyst complexes are applied.

The efficiency of additive is determined by its chemical structure. Depending on the type of polymer applied in the binder matrix, one kind of additive will be chosen. Ferryacetyl acetonate, ferryoctoate and different types of amine are used in CRP based on PU, because of their effect on pot life. Certain types of compounds like acetyl acetone, tetracycline and substituated aniline retard the curing reaction, but at the same time provide networking over a suitable period of time, ensuring the required propellant quality [3, 4, 5]. TC, shown in Fig.1, can form a metal complex across carboxyamide (ring A) or with hydroxyl-keto part of the rings (B, C)

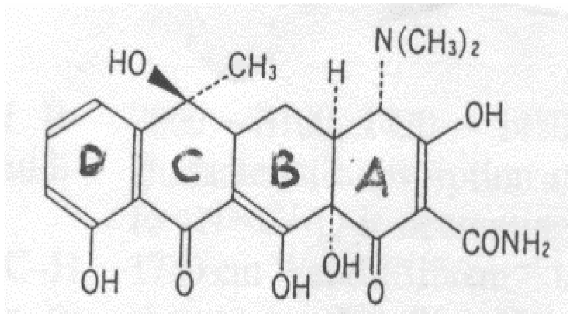

Figure 1. Tetracycline

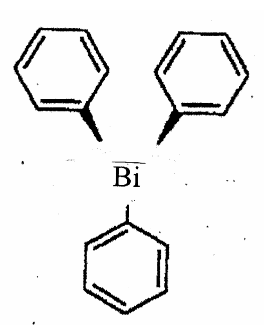

Figure 2. Triphenyl bismuth

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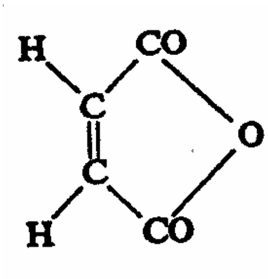

Figure 3. Maleic anhydride

For cure rate controlling of propellants based on hydroxy-terminated polybutadiene (HTPB) prepolymer, the catalyst system comprising organo-metallic compounds and carboxylic acids or compounds convertible thereto by reaction with active hydrogen (anhydride carboxylic acids) are used. Triphenyl bismuth and maleic anhydride are the most frequently used (Figure 2 and 3), as well as their combination with magnesium or calcium oxide [6]. In addition to TC, aniline and its derivative are efficiently used as this type of additives for carboxyterminated polybutadiene (CTPB). Components for improving mechanical properties such as bonding agents have significant influence on the viscosity by means of chemical structure and bond creation with propellant components [7]. These compounds ensure pot life control and short curing period, resulting in energy saving and capacity amplification in propellant production.

Experiment

Two basic types of propellants, with different binders were used for the experiment:

- Based on hydroxyterminated polybutadiene (HTPB), cured with isophorone-diisocyanate (IPDI) or dymeril-diisocyanate (DDI). Bimodal mixture of AP with mean particle sizes of 200 μm and 7 – 8 μm 72 mas.% was used as oxidizer. Bimodal mixture of Al, the burning rate stabilizer, with mean particle sizes of 15 μm and 30 μm 13 mas.% as metal component which, owing to its density (> than AP) helps overcome the difficulties caused by increased viscosity. Tris-1-(2-methylaziridinyl) phosphineoxide (MAPO) and 2,2'-methylenebis [6-(1,1–dimehylethyl)–4-methylphenol] (AO22) were used as bonding agent and antioxidant, respectively.
- Based on the mixture of polyetherpolyols (diols – Pluriol 2000 and triols – Arcol 1131) in 70 : 30 ratio, cured with toluene-diisocyanate (TDI) – PU propellants – containing 73 mas.% of the same bimodal mixture of AP, where ferryacetylacetonate $Fe(AA)_3$ was used as the curing catalist. These compositions were nonaluminized and triethylene tetramine (TET) and N-phenyl-β-napftylamine (FβNA) were used as bonding agent and antioxidant, respectively.

The dioctyladipate (DOA) was the plasticiser in all propellants. The two types of HTPB were used as the basic prepolymer: [1)] R-45HT polymer and [2)] R-45M polymer, which were derived by 1) radical and 2) anionic polymerization.

The propellant compositions based on HTPB/IPDI and HTPB/DDI were made first without the oxides of iron, Fe_2O_3, and copper, $CuCr_2O_4$, as burning rate catalysts and then including them; these compositions can be seen in Table 1.

Table 1. CRP/HTPB - no additives (control base)

No Batch	Curing agent (CA)	Curing agent's part [DSD]	Fe_2O_3 [%]	$CuCr_2O_4$ [%]
1^1	DDI	21,62		
2^1	DDI	21,62	1,0	
6^1	IPDI	7,49		
9^2	IPDI	8,49	1,0	
13^2	IPDI	8,49		1,0

In Tables 2 and 3 the same propellants are shown with different types of additives included.

Table 2.: CRP/HTPB/1 % Fe_2O_3 plus additives

No Batch	CA	RM-410 [%]	TC [%]	PG [%]	TFBi [%]	MA [%]	MgO [%]
3^1	DDI		0,2				
4^2	DDI	0,2					
5^2	DDI				0,025	0,025	0,025
7^1	IPDI		0,4				
8^1	IPDI		0,2				
10^2	IPDI		0,1				
11^2	IPDI				0,025	0,025	0,025
12^2	IPDI				0,04	0,04	0,04
18^2	IPDI			0,15			
19^2	IPDI				0,05		0,05
20^2	IPDI				0,02	0,02	
21^2	IPDI	0,2					

Table 3. CRP/HTPB/1 % $CuCr_2O_4$ plus additives

No Batch	CA	RM-410 [%]	TC [%]	PG [%]	TFBi [%]	MA [%]	MgO [%]
14^2	IPDI		0,2				
15^2	IPDI				0,025	0,025	0,025
16^2	IPDI	0,2					
17^2	IPDI			0,1			

PU propellants were mixed with iron (III) oxide as shown in Table 4.

Table 4: CRP/PU/1 % Fe_2O_3 plus additives

No Batch	Fe_2O_3 [%]	TC [%]	TFBi [%]	MA [%]	$Fe(AA)_3$ [%]	HAA [%]
22	1				0,03	0,009
23	1				0,03	
24	1	0,2			0,03	
25	1		0,03	0,03	0,03	

All batches were homogenized in the vertical planetary mixer, under vacuum, at 50 °C, because of the beneficial effect that the lower mixing temperatures have on the level of viscosity [8]. The HTPB propellants were cured for 120 h, while PU propellant curing lasted for 72 h, at 70 °C. The viscosity changes of all batches during this period were observed and the possibility of reducing the viscosity of propellants from Tables 1 - 4, including iron-oxide (Fe_2O_3) and copper-chromite ($CuCr_2O_4$) as burning rate catalysts, by some of the represented additives (TC, PG, HAA, RM-410, TFBi, MA, MgO) was examined. Considering the fact that this effect is related to the curing process, it is expected that it is also reflected on the propellant's mechanical characteristics, [9]. Propellant viscosity change over time due to the curing process is determined by Brookfield HBT viscometer, at spindle revolution of 5 min^{-1}, and test temperature of 50 °C.

Results and discussion

CRP containing catalysts Fe_2O_3 or $CuCr_2O_4$ show sharper time–viscosity change dependence than ones without them, decreasing pot life. Viscosity changing rate depends on the curing agent (CA) type. Propellants based on HTPB/IPDI show smaller viscosity progress than HTPB/DDI propellants [10]. In the presence of catalyst all negative effects become significant, which can be seen in Fig.4. The greatest growth has been attained for No. 2, a combination of DDI/ferryoxide. In case of IPDI/any, catalyst viscosity does not differ significantly.

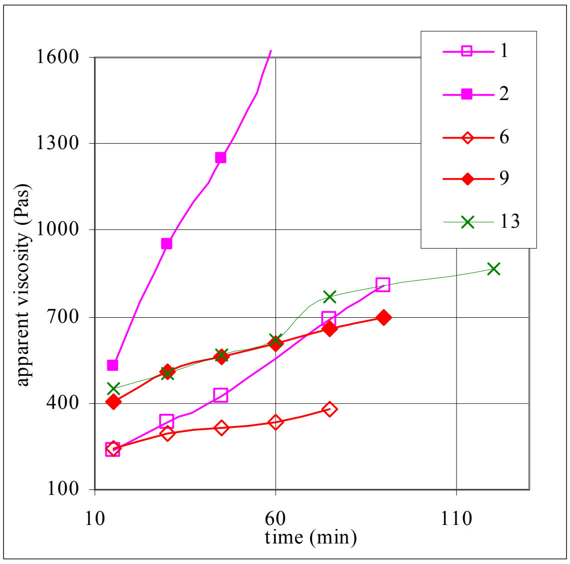

Figure 4. Effect of Fe_2O_3, $CuCr_2O_4$ and CA type on viscosity

In Fig.5, the effect of TC in HTPB/IPDI/Fe_2O_3 propellants is shown. Great growth of viscosity from the basic No. 6 to No. 2 is apparent, but by adding TC, pot life is extended and viscosity values at the beginning reduced. Furthermore, it is better to use smaller amount of TC - 0,1 mas.% or 0,2 mas.%, (No. 8 and No. 10) than 0.4 mas.% (No. 7). The optimal amount of TC depends on the type and content of the propellant components.

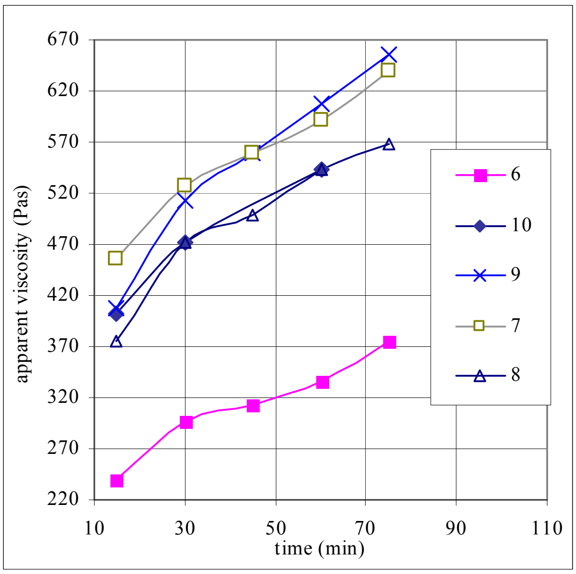

Figure 5. Effect of TC on viscosity of HTPB/IPDI propellants

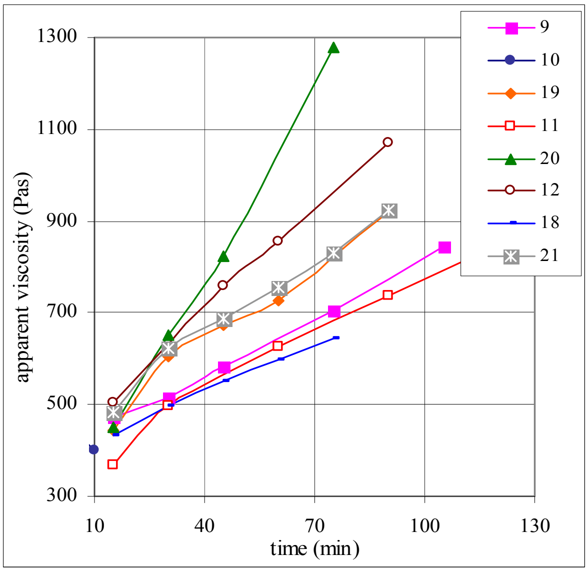

Figure 6. Effect of different additives on HTPB/Fe_2O_3 propellants

Compositions based on HTPB/IPDI including Fe_2O_3 are shown in Fig.6. Propellant 9, with no additives is the control one and the others are estimated in relation to it. In addition to TC (No. 10), other additives also have positive effect on reducing the viscosity feature, such as mixture of TFBi, MgO and MA (No. 11) and pyrogaloll (No. 18). Diester of phosphoric acid, RM-410 (No. 21), such as the skipping of MgO or MA has a negative effect, although these combinations are mentioned in the references in a positive light [6]. Consequently, the final effect depends on the content of other components.

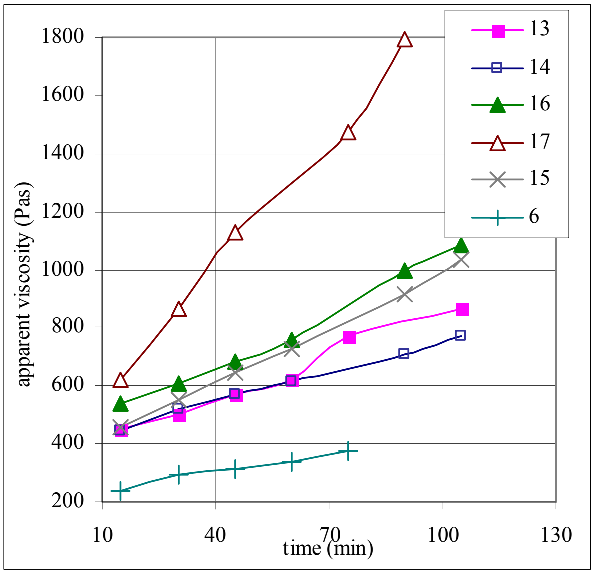

Figure 7. Effect of different additives on HTPB/$CuCr_2O_4$ propellants

The best effect in compositions with $CuCr_2O_4$ (Fig.7) is shown by TC (No. 14) – the viscosity values are lower than those for composition with no additive (No. 13). PG (No. 17) has been especially unfavourable, and the mixture of TFB, MA and MgO (No. 15), as well as phosphor acid diester, RM-410 (No. 16), showed no effect on reducing the viscosity value.

Significant effect of TC is detected in HTPB/DDI propellants with Fe_2O_3, (see Fig.8), so the viscosity difference between propellants based on DDI and IPDI curing agents is greatly decreased. The rise of values of viscosity can be illustrated by the following row of additives: TC (No. 3)<RM-410 (No. 4)<(TFB+MgO+MA) (No.5). Favourable propellants can be limited by compositions No. 1 (»empty«) and No. 2 (with catalyst). According to the references [3], a good effect of TC has been confirmed in HTPB/DDI/Fe(AA)$_3$ propellants.

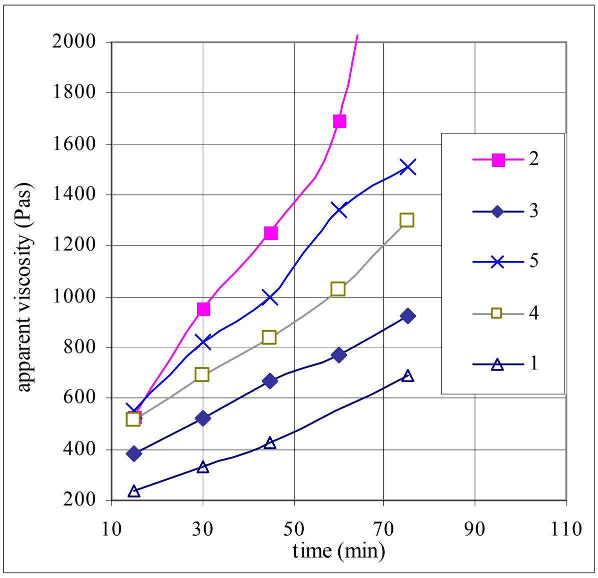

Figure 8. Time-depending viscosity of CRP/HTPB/DDI/Fe_2O_3

When Fe(AA)$_3$ is used as curing rate agent in the polyether diols and triols mixtures as classical polyurethane propellants, it plays a big role in the viscosity change (pot life). The TC, HAA and the TFBi and MA mixture effect on the viscosity is presented in Fig.9. No. 23 is the control composition, containing only Fe(AA)$_3$. The positive effect was shown in compositions No. 25 (the mixture of TFBi and MA) and No. 22 (with HAA). It is interesting to note that adding TC to PU propellants (No. 24) greatly reduced the pot life.

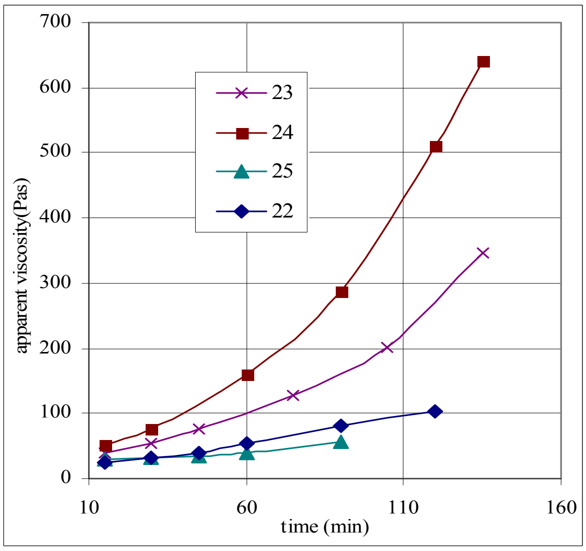

Figure 9. Viscosity time dependence for PU propellant

To determine whether interaction between the additives and binder components or Fe ions from the catalyst exists, four different binders the same as the propellant binder were made, with additives shown in Table 5 and the viscosity values in Fig.10.

Table 5. PU binders

No.	TC [%]	TFBi [%]	MA [%]	Fe(AA)$_3$ [%]	HAA [%]
23B	-	-	-	0,05	-
25B	-	0,02	0,02	0,05	-
24B	0,18	-	-	0,05	-
22B	-	-	-	0,05	0,009

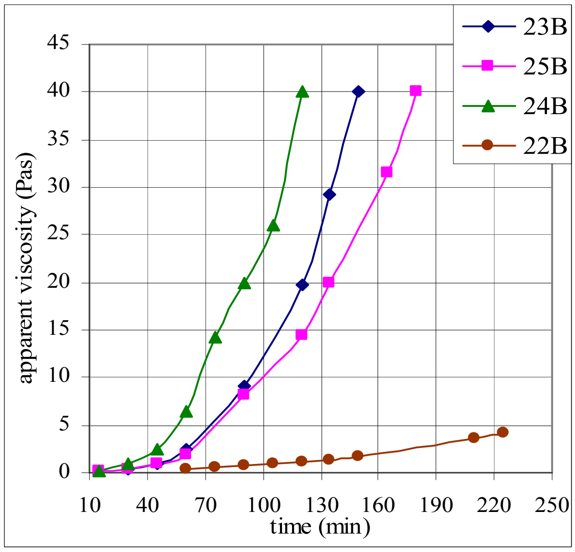

Figure 10. Binder PU / additive propellants viscosity changing

Results of the PU binder (Fig.10) examination have confirmed that TC realises secondary bonds with the polymer across oxygen atoms in the polymer chain and the viscosity growth is quickly elevated, in case of No. 24B. The most suitable additive is believed to be the HAA (No. 22B). Further examinations of the interactions mentioned above included the mechanical characteristics of these four binders, shown in Table 6.

Table 6. Mechanical characteristics of PU binders

No	Additive	σ_p [daN/cm^2]	ε_p [%]
23B	-	3,41[1]	1353[1]
25B	TFBi, MA	3,61	1027
24B	TC	2,78	828
22B	HAA	2,55	980

σ_p-maximum stress at rupture, ε_p-elongation at rupture
[1])-the sample has not been broken

The lower values of mechanical characteristics indicate that TC reacts with –NCO groups and in that manner terminates the polymer chains, neutralizing further ramification and decreasing polymer network.

Conclusion

Applying a small amount of burning rate catalyst Fe_2O_3 or other iron and chrome compounds, will generate the increase of propellant viscosity, shortened pot life and preclude the application of some compositions. TC, the well-known antibiotic, can form complexes with Fe_2O_3 or $CuCr_2O_4$, reducing the viscosity and prolonging the pot life, which is the consequence of the chemical structure. This is more striking in case of HTPB/DDI propellants than HTPB/IPDI propellants.

On the other hand, considering the propellants based on HTPB/IPDI, it can be noticed that the mixture comprising catalysts TFBi, MA and MgO has less effect on the viscosity than TC. The optimum components content, such as their mutual ratios, are determined by the propellant composition.

With the TFBi, MgO, MA mixture catalyser mixture HTPB/IPDI curing process becomes significantly faster, with the favourable pot life. This curing method contributes to reducing the loss of energy and increasing the capacity, which is important in small grain production.

In addition to the most efficient additive, HAA, a successful drop of viscosity in PU propellants can be achieved using the mixture of TFBi, MgO and MA.

References

[1] Hoffman, E. Richard, Cure Rate Inhibitors for Ferrocene-Containing Proppelants, US Pat. 4,352,700, Okt.5, 1982.

[2] Petrić, M. Tasić, D. Uticaj 1,3-diferocenil-1-butena na brzinu sagorevanja kompozitnih raketnih goriva, Naučnotehnički Pregled, Vol. LI, br. 6, 2001.

[3] Sanden, R. Tetracycline, an Aditive for Increasing Pot Life of Composite Propellants, Jahresagung 1982, 641-654.

[4] Tokui, H. Iwama, A. Pot Life Problem and its Measure with a Reduced Smoke Propellant, Production, Propellants, Explosives, Pyrotechnics 16, 105-109, 1991.

[5] Petrić, M. Uticaj tipa umreživača na viskozitet kompozitnih raketnih goriva na bazi karboksiterminiranih polibutadienskih prepolimera, Naučnotehnički Pregled, Vol. L, br. 4-5, 2000.

[6] Graham, W. H. Shepard, I. G. Control of Cure Rate of Polyurethane Resin Based Propellants, US Pat. 4,110,135, 1978.

[7] Petrić, M. Bonding agensi za kompozitna raketna goriva, Vojnotehnički glasnik, 2003, 1, 51-62.

[8] Petrić, M. Rodić, V. Mehaničke i reološke osobine kompozitnih raketnih goriva na bazi hidroksiterminiranog polibutadiena, VTI-04-01-0295, VTI Beograd, 2002.

[9] Petrić, M. Rodić, V. Vreme livljivosti (pot life) kompozitnih raketnih goriva, VTI-04-0378, VTI Beograd, 2004.

[10] Rodić, V. Petrić, M. The effect of curing agents on solid composite rocket propellant characteristics, Naučnotehnički Pregled, Vol. LV, No. 1, 2005.

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Uticaj aditiva na karakteristike kompozitnih raketnih goriva

U radu se ispituje uticaj različitih aditiva na brzinu promene viskoziteta kompozitnih raketnih goriva (KRG) na bazi hidroksiterminiranog polibutadiena (HTPB), umreženih izoforon-diizocijanatom ili dimeril-diizocijanatom koja sadrže ferioksid, odnosno bakarhromit i KRG na bazi poliuretana (PU), umrežavanih sa toluen-diizocijanatom sa dodatkom ferioksida. Analizirana je vremenska promena prividnog viskoziteta KRG i uticaj na proces umrežavanja u zavisnosti od vrste i količine aditiva: tetraciklina, (TC), pirogalola (PG), diestra fosforne kiseline (RM-410), acetilaceton (HAA) i smeše katalizatora umrežavanja koju čine trifenilbizmut (TFBi), anhidrid maleinske kiseline (MA) i magnezijum oksid (MgO).

Ključne reči: **kompozitno raketno gorivo, viskozitet, aditivi, uticaj aditiva, tetraciklin, pirogalol, trifenilbizmut, acetilaceton.**

Влияние аддитива на характеристики многокомпонентных ракетных топлив

В настоящей работе исследуется влияние различных аддитивов на скорость изменения вязкости многокомпонентных ракетных топлив (МРТ) на базисе гидрокситерминированного полибутадиена (ГТПБ), комбинированных со сеточным изофорон-диизоцианатом или димерил -диизоцианатом, которые содержат ферриокисел, т.е. медьхромит и МРТ на базисе полиуретанов (ПУ), комбинированных со толуен- диизоцианатом со добавлением ферриокисла. Здесь анализировано временное изменение кажущейся вязкости МРТ и влияние на процесс комбинирования в зависимости от типа и количества аддитивов: тетрациклина (ТЦ), пирогаллола (ПГ), диэфира фосфорной кислоты (РМ-410), ацетилацетона (ХАА) и смеси катализаторов комбинирования, в которой находятся - трифенилвизмут (ТФБи), ангидрид малеиновой кислоты (МА) и окисел магния (МгО).

Ключевые слова: многокомпонентное ракетное топливо, вязкость, аддитивы, влияние аддитивов, тетрациклин, пирогаллол, трифенилвизмут, ацетилацетон.

Influence des additifs sur les caractéristiques des propergols composites

Dans ce papier on a présenté les essais sur l'influence de différents additifs à la vitesse de changement de la viscosité chez les propergols composites à la base du polybuthadène hydroxyterminé et lié par isophorone-diisocyanate ou dyméril-diisocianate qui contiennent oxyde de fer ou bromure cuprique ainsi que des propergols composites à la base du polyuréthane liés par toluène-diisocyanate contenant oxyde de fer. On a analysé le changement temporel de la viscosité et les effets sur le procédé de liage selon le type et la quantité des additifs :tétracycline(TC), pyrogallol (PG), diester acide phosphorique (RM-410), acétylacétone (HAA) et le mélange des cataliseurs de liage, composé par triphényl bismuth, anhydride maleic (MA) et magnésium oxyde (MgO).

Mots clés: **propergol composite, viscosité, additifs, influence des additifs, tétracycline, pyrogallol, triphényl bismuth, acétylacétone.**