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Influence of Composition on the Processability of Thermobaric Explosives

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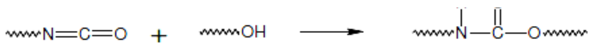
The influence of the composition of cast composite thermobaric explosives on their processability was investigated. According to the experimental plan, 10 different thermobaric PBX explosive compositions were produced by casting technology. The content of three components was varied: thermosetting hydroxyterminated polybutadiene binder (15 – 20 wt.%), ammoniumperchlorate (0 - 20 wt.%), and magnesium participation in a total metal content of 30 wt.%, i.e. 0 - 30 wt.% of aluminium was replaced by pyrolitic magnesium.
The impacts of compostion and curing time on viscosity were examined. It was analyzed how the changes of component content affect the viscosity-time dependance for the three uppermentioned components taken separately as well as combined. The densities of the samples taken from different segments of explosive charges were determined according to the standard method MIL 286B, and then the porosities were determined as well.

Key words: **thermobaric explosives, cast explosives, composite explosives, PBX, ammoniumperchlorate, aluminium, magnesium, viscosity, density, porosity, processability.**

Introduction

SOLID thermobaric explosives (TBE) are hybrid explosive compositions having characteristics of both - high explosives and fuel/air explosives. The detonation of thermobaric explosives generates a shock wave of substantially longer duration than a shock wave generated by conventional high explosives, increasing the lethal radius [1]. Being mixtures of a crystalline high explosive and a polymeric binder, they belong to the family of plastic bonded explosives (PBX). Immediately after preparation, they are directly loaded into a corresponding weapon by cast technology and, by programmed crosslinking at a higher temperature, they turn into a solid explosive charge with rubber-elastic characteristics.

Modern cast composite thermobaric explosives, similar to composite solid propellants, consist of nitroamine as a crystal explosive component, a polymeric binder, an oxidizer and a fuel component (metal powder). The polymeric binder, which constitutes 15-20% of the explosive composition, generally consists of a telechelic liquid prepolymer, a curing agent, a plasticiser, a bonding agent, and an antioxidant [2]. All the ingredients, except the curing agent (diisocyanate), are mixed thoroughly to ensure a high degree of homogeneity of the mixture. The desired quantity of diisocyanate is added and mixed thoroughly just before casting. The main reaction between the hydroxyl telechelic polymers and the isocyanate compounds is given below (1). The cure reaction between the hydroxyl groups of hydroxyterminated polybutadiene (HTPB) and the cross linker isocyanate groups causes the viscosity of the slurry to increase with time [3].


(1)

In a reactive polymeric system such as the cast composite explosive slurry, after the addition of a curing agent, rheology depends on a number of variables e.g. time, temperature, deformation rate, filler concentration, chemical formulation, reaction kinetics, etc, which makes a rheological characterization very complex [4]. The mixed explosive must be cast before the curing reaction has progressed to the point beyond which casting is no longer possible [3]. The time required to reach this state is generally called the "pot life" - the time the mixture remains sufficiently fluid to permit processing and casting. It is important that viscosity of cast composite explosives changes slowly during time, so their "pot life" is long enough. Slurry maintained at higher temperature gets cured fast, which results in fast decrease of the casting rate and also makes the pot life shorter [2]. It generally varies from 4 to 5 hours depending upon the reaction kinetics and a composition of the curing mass. The polyurethane cure reaction should neither be too fast, nor too slow. The viscosity of PBX should not be too high to obtain a better dispersion of the components in it, and not too low to avoid their sedimentation. The time dependence of the viscosity of uncured PBX is a nonlinear function, because the change of viscosity is induced by a running reaction of the polymer binder cross-linking. But, in the first 2-3 hours, it is favorable that viscosity changes very slowly. A good understanding of the rheology is very important for process design and control.

Aluminum, commonly used as a fuel component due to its high heat of combustion, cost and availability, has a high

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ignition temperature, 2200 K. Burning of all the alluminium to completion requires maintaining the hot environment which can be maintained if it is supported by the combustion of other easily combustible metals and oxidizers, such as ammoniumperchlorate (AP), much easier to ignite (AP has an ignition temperature of 250°C). The combustion of AP produces hot gases to support metal burning, so higher combustion efficiency can be obtained. Nowadays, Al is used in mixtures with magnesium for more complete combustion [5, 6].

Magnesium, on the other hand, has the capability to catalyze some polymerization reactions, and it is reported that it has influence on HTPB polymerization [7, 8], used as a binder in cast composite explosive compositions examined in this investigation, so it is interesting to examine its effect on their rheology.

Hydroxyterminated polybutadiene has lower viscosity than carboxyterminated and polybutadiene-acrilonitrile co-polymers; therefore, it represents an excellent choice for a binder. Good castabillity is hard to be obtained when a system consists of more than 80% of a solid phase. Thus, it is necessary to provide good particle packaging, which is possible with multimodal granulation of solid ingredients. In these compositions, it is most suitable to use crystalline explosives with a bimodal or a threemodal mixture of fine (0-100 μm) and coarse fractions (200-400 μm and 200-800 μm), reducing the viscosity of uncured PBX.

This paper refers to the influence of composition on the processing of cast composite explosives in which aluminum is partially replaced by pyrolytic magnesium (60-85 μm). According to the plan of the experiment, by the technological process of casting, 10 different explosive compositions were prepared, with varied mass concentrations of the following three components:

- thermoreactive polymer binder - HTPB from 15 to 20%,
- ammoniumperchlorate - AP from 0 to 20%,
- proportion of magnesium and aluminium were varied to form a total metal content of 30%.

For this kind of cast composite explosives that belongs to IM (Insensitive Munition) group of energetic materials, it is important to achieve minimal porosity, because such places as voids or gas cavities inside of an explosive charge could represent a potential risk of the "hot-spot" initiation or ignition sites [9]. Explosive non-homogeneity leads to discontinuity of mechanical and thermal energy distribution behind the shock wave front. Local regions of high energy density, hot spots, can be formed in an explosive charge as a response to a shock, or while handling or mechanically processing these explosive charges. If sufficient thermal energy is produced, then hot spots can burn outwards into the bulk of the explosive leading to a possible growth of reaction, i.e. unplanned initiation. Therefore, this work also comprises density and porosity examination of chosen thermobaric explosive compositions.

Experiments and discussion of the results

Within this investigation, 10 different explosive compositions were prepared. Labels and formulations for produced thermobaric explosives are given in Table 1. They all have excellent thermobaric effects, investigated in previous examinations [10]. It was planned to prepare, as a reference, composition TBE-1, because of its excellent properties, according to earlier studies [11, 12]. As a standard (averaged) composition, TBE-10 was prepared with average mass concentrations of the components for compositions TBE-2 - TBE-9.

Table 1. Composition of the examined explosive charges

Explosive composition's labels	Mass concentrations of components (%)				
	HMX	AP	Al	Mg	HTPB binder
TBE-1	50	0	30	0	20
TBE-2	45	10	27	3	15
TBE-3	45	10	21	9	15
TBE-4	41	10	27	3	19
TBE-5	41	10	21	9	19
TBE-6	35	20	27	3	15
TBE-7	35	20	21	9	15
TBE-8	31	20	27	3	19
TBE-9	31	20	21	9	19
TBE-10	38	15	24	6	17

The following raw materials were used for the preparation of explosive charges:

- octogen (HMX, "DINO" - Norway, Class A/C) according to MIL-H-45444,
- aluminum of an average diameter of 5 μm, according to MIL-STD-129,
- magnesium of an average diameter of 65 μm (manufacturer ECKA GRANULES - Austria), according to MIL-DTL-382D,
- ammoniumperchlorate, 7-10 μm,
- polymeric binder, based on hydroxyterminated polybutadiene cured by isophorone-diisocyanate (IPDI) [13, 14], including additives (plasticizer, antioxydant, and bonding agent). The stochiometric ratio of the curator to binder (NCO/OH ratio) was fixed at 0.975 for this formulation.

The experimental explosive compositions are prepared according to [15], in a vertical planetary mixer under vacuum, at 50°C. The technological parameters of preparing all TBE compositions were the same (order of dosing components, stirring speed and time of homogenization, as well as the mixing time of the composite mixture after adding the curing agent). After homogenization, explosive is directly poured into the previously prepared molds (diameter 30 mm, height 160 mm). After crosslinking and mold dismantling, the experimental samples were obtained to determine the density.

The dependence of viscosity on composition during time was examined for the mentioned 10 thermobaric explosive compositions. After the addition of the cross-linking agent, the explosive mixtures were homogenized for 10 more minutes, and then the samples were taken.The viscosities are measured in the Brookfield's viscometer type RVT at 50°C, with the measuring spindle speed of 5 min^{-1}, every 15min. The obtained viscosity values are shown in Table 2. The viscosity - time dependencies for the prepared compositions are shown in Fig.1.

Table 2. Viscosities of TBE compositions

Time (min)	Dynamic viscosity η (Pa·s)									
	TBE-1	TBE-2	TBE-3	TBE-4	TBE-5	TBE-6	TBE-7	TBE-8	TBE-9	TBE-10
15	39.2	156.4	288.0	64.0	93.2	228.4	324.0	82.0	124.0	134.0
30	42.0	166.0	304.4	64.0	94.0	244.0	344.0	80.8	126.0	136.0
45	48.0	168.3	312.0	67.6	97.6	257.2	365.2	84.0	132.0	139.2
60	54.8	178.0	320.0	70.0	99.6	269.2	378.4	85.6	136.4	144.4
75	56.8	180.8	332.0	71.2	103.2	274.8	395.2	90.0	144.0	149.2

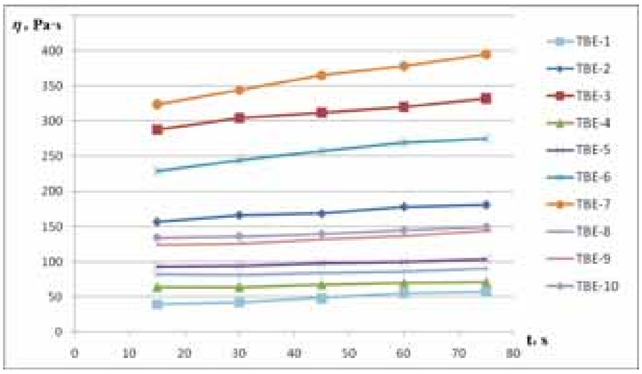

Figure 1. Dependence $\eta = f(t)$ diagrams for the investigated thermobaric compositions

Nearly linear dependences $\eta = f(t)$ are obtained for TBE composite mixtures. It can be concluded that all compositions have good rheological properties since they have almost horizontal curve positions (Fig.1) and show a moderate viscosity increase in time. They all remain castable long enough, so they have a favorable processing time.

The influence of the individual components is evident in separate diagrams for the considered compositions, which is shown in the following figures The representative compositions were grouped in order to give a comparative review of the effect intensity of various factors on the viscosity, and thus the rheological behavior of cast composite explosive compositions. In the given comparisons, there is $\eta = f(t)$ diagram for TBE-1, which is placed significantely below other curves, and it shows how the processability of other compositions is changed.

TBE-2 and TBE-3 compositions (Fig.2) illustrate the influence of Mg content for the same concentrations of other components: a greater amount of Mg causes a higher viscosity.

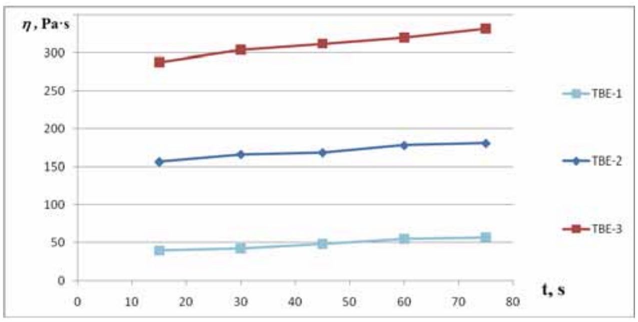

Figure 2. Dependence $\eta = f(t)$ diagrams for TBE-1, TBE-2 and TBE-3

A significant difference in viscosity is apparent for TBE-3 and TBE-4 compositions (Fig.3) due to several factors: different amounts of the binder (reducing the amount of the binder results in a significant viscosity increase), 4% of HMX is replaced with Al (the same mass has a smaller volume - ρ(HMX)=1.91 g/cm^3, ρ(Al)=2.7 g/cm^3), and different amounts of Mg. However, satisfying processing characteristics still remains.

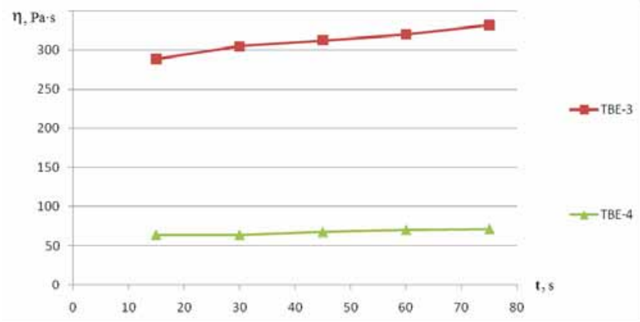

Figure 3. Dependence $\eta = f(t)$ diagrams for TBE-3 and TBE-4

The TBE-7 and TBE-8 samples provide an insight into the combined effect of Mg and the binder content (Fig.4): the composition with less binder and more Mg, besides much higher value of viscosity, shows its rapid increase with time. TBE-8 composition, which has approximately the same content of the binder, HMX and AP as TBE-1, has higher viscosity, apparently due to the presence of Mg and a bigger amount of Al instead of HMX (having different densities).

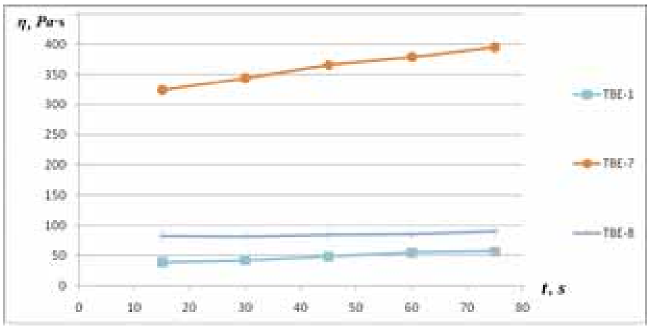

Figure 4. Dependence $\eta = f(t)$ diagrams for TBE-1, TBE-7 and TBE-8

TBE-4 composition has viscosity values between the values for TBE-1 and TBE-8 (Fig.5). As TBE-4 has the same amount of the binder, Al and Mg as TBE-8 has, it can be concluded that TBE-8 has higher viscosity due to AP content increase at the expense of reducing the amount of HMX. The reason for that are different densities of ingredients (ρ(HMX)=1.91 g/cm^3, ρ(AP)=1.95g/cm^3).

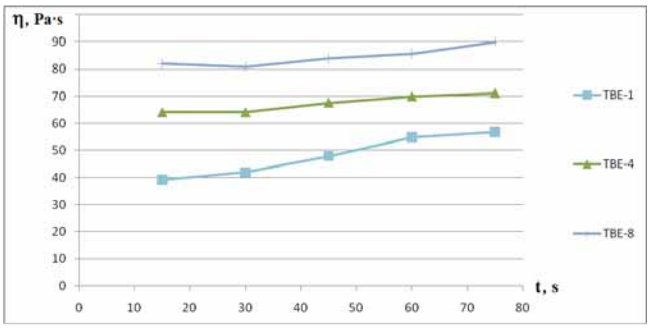

Figure 5. Dependence $\eta = f(t)$ diagrams for TBE-1, TBE-4 and TBE-8

If we observe a paralel comparison of the viscosities for TBE-2 and TBE-3, and also for TBE-8 and TBE-9, we can notice that the influence of a higher Mg content is more evident for the viscosities of the compositions that contain less binder, ie. the difference between TBE-2 and TBE-3 viscosity is larger than the difference between TBE-8 and TBE-9 viscosity (Fig.6), In other words, in a system containing less binder, the same amount of Mg is more concentrated. That is why the viscosity gradient is higher.

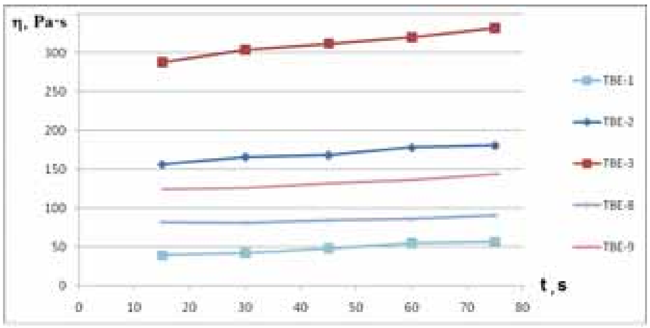

Figure 6. Dependence $\eta = f(t)$ diagrams for TBE-1, TBE-2, TBE-3, TBE-8, and TBE-9

It is important to have an insight in the rheological behavior of an "average" compostiton, TBE-10, and to compare it to "equidistant" compositions, for example to TBE-2 and TBE-9 (Fig.7), or to TBE-5 and TBE-6 (Fig.8). During the measuring time, the viscosity values for TBE-10 were between the values for TBE-2 and TBE-9, but significantly closer to TBE-9. Also, the viscosity values for TBE-10 were between the values for TBE-5 and TBE-6, but significantly closer to TBE-5. This confirms the explanations of combined effects.

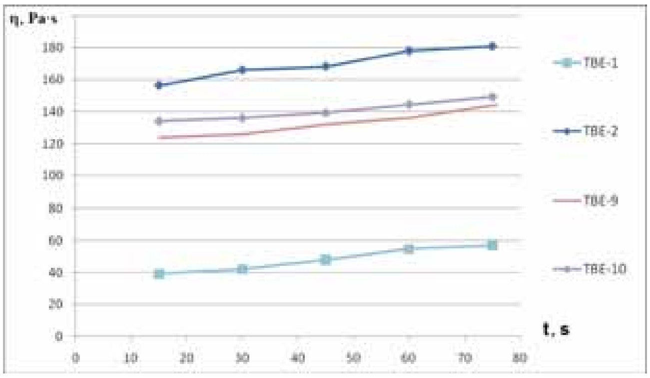

Figure 7. Dependence $\eta = f(t)$ diagrams for TBE-1,TBE-2,TBE-9 and TBE-10

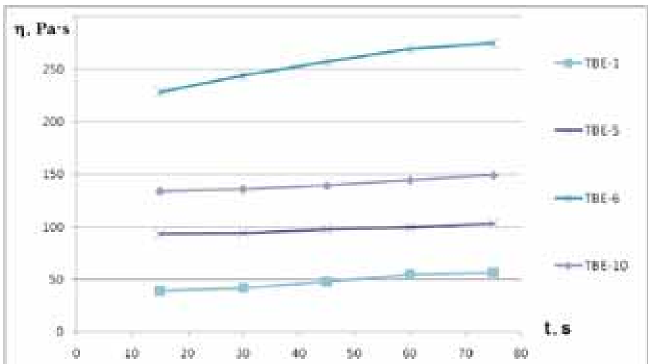

Figure 8. Dependence $\eta = f(t)$ diagrams for TBE-1,TBE-5, TBE-6 and TBE-10

For several selected representative compositions, densities were determined according to MIL 286B method, measuring the masses of the samples from the upper, middle and lower segment of the explosive charge on the Mohr's scale in toluene at 25°C. The experimentally obtained values were then compared to the theoretical density values calculated according to (2):

$$1/\rho_t = W_A/\rho_A + W_B/\rho_B \tag{2}$$

where:
ρ_t - theoretical value of density,
W_A, W_B - mass fraction of the components,
ρ_A , ρ_B -density of the components.

The segment density values and their averages are given in Table 3. There is no significant difference between the values of density in different segments, ie. the densities of segments are very close to the average values. This indicates a very good homogeneity of explosive charges, which is important for good detonation parameters.

Table 3. Densities of TBE charges by segments and their average values

TBE charge	TBE-1	TBE-2	TBE-3	TBE-8	TBE-9
ρ_1	1.672	1.755	1.705	1.694	1.659
ρ_2	1.668	1.754	1.699	1.698	1.664
ρ_3	1.670	1.751	1.701	1.700	1.666
ρ_{sr}	**1.670**	**1.753**	**1.702**	**1.697**	**1.663**

ρ_1 - density of the specimen from the upper segment,
ρ_2 - density of the specimen from the midle segment,
ρ_3 - density of the specimen from the lower segment,
ρ_{sr} – average density

The theoretical values and the experimentally obtained densities, as well as porosities, are given and compared in Table 4. The porosity values were calculated according to (3):

$$v = (1 - \rho_e/\rho_t)100(\%) \tag{3}$$

where:
v - porosity,
ρ_e - experimental value of density.

Table 4. Theoretical and average experimental densities and porosities of TBE charges

	TBE composition (%) HMX/AP/Al/Mg/HTPB	ρ_T (g/cm^3)	ρ_e (g/cm^3)	v (%)
TBE-1	50/0/30/0/20	1.705	1.670	2.03
TBE-2	45/10/27/3/15	1.773	1.753	1.11
TBE-3	45/10/21/9/15	1.734	1.702	1.83
TBE-8	31/20/27/3/19	1.709	1.697	0.68
TBE-9	31/20/21/9/19	1.672	1.663	0.57

The measured densities are close to the theoretical values, and porosities are low, whaich is very convenient for this type of explosives. It can be noted that porosities are getting significantly lower in the presence of fine granulation particles of AP and Mg, caused by better possibility of particle packaging. Also, a higher binder content has a favorable effect on porosity, since solid phase particles are better incorporated into a larger quantity of the polymer matrix. TBE-9 has the lowest porosity due to its highest content of AP, Mg and HTPB binder.

Conclusion

The investigation of processability is done for 10 different thermobaric PBX explosive compositions, previously prepared. Viscosity-time dependences, densities and porosities are determined for the examined samples. The greatest effect on the rheological properties of the examined compositions has the mass concentration of the binder, then the participation of Mg in the total metal content, and the concentration of fine aggregate AP at the expense of reducing the content of coarse fraction HMX. A higher amount of Mg in compositions with the same content of other components causes faster growth and higher values of viscosity, thus reducing the processing time (castability) of the compositions, while a larger content of the binder and replacing HMX by AP have a favorable effect. For the selected representative compositions, the measured density values have shown to be very close to the theoretical values. There are no significant variations between the values of density in different segments of experimental explosive charges, so it can be concluded that a very good homogeneity is achieved. The porosities of the examined explosives are low, which is a good quality for this kind of explosives. The values of porosity are lower for the compositions containing a higher percentage of AP and Mg, and also having a higher content of the HTPB binder. TBE-4, TBE-5, TBE-8, TBE-9 and TBE-10 compositions have a moderate viscosity gradient and, therefore, good rheological properties. They all remain castable long enough, so they have favorable processing characteristics, especially TBE-8 and TBE-9, having also the lowest porosities after curing. Taking this into consideration as well as a good thermobaric effect that can be predicted based on their ingredients content, the explosive compositions mentioned above represent good candidates for industrial production.

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Uticaj sastava na preradljivost termobaričnih eksploziva

U radu je ispitan uticaj sastava na preradljivost termobaričnog livenog kompozitnog eksploziva. Prema planu eksperimenta, tehnološkim postupkom livenja izrađeno je 10 različitih sastava termobaričnih PBX eksploziva kod kojih je variran maseni udeo tri komponente: termoumrežavajućeg veziva na bazi hidroksiterminiranog polibutadiena (15-20%), amonijumperhlorata (0-20%), i u ukupnoj količini od 30% metala, 0-30% aluminijuma je zamenjeno pirolitičkim magnezijumom.

Ispitana je zavisnost viskoziteta od sastava i od vremena. Analiziran je intenzitet uticaja promene udela pojedinačnih komponenata, kao i njihovi kombinovani uticaji, na promenu viskoziteta s vremenom. Gustine uzoraka uzetih iz različitih segmenata eksplozivnog punjenja određene su prema standardnoj metodi MIL 286B, a potom su određene i poroznosti.

Ključne reči: **termobarični eksplozivi, liveni eksplozivi, kompozitni eksplozivi, PBX, amonijumperhlorat, aluminijum, magnezijum, viskoznost, gustina, poroznost, preradljivost.**

Влияние состава на перерабатываемость (технологичность) термобарических взрывчатых веществ

В данной работе исследовано влияние состава на переработку (технологичность) термобарических литых композитных взрывчатых веществ. В соответствии с планом эксперимента, технологическим процессом литья производится 10 различных композиций термобарических АТС взрывчатых веществ, где разнообразная массовая доля из трёх составляющих: термосетевых связующих на основе гидрокситерминированного полибутадиена (15 - 20%), перхлорат аммония (0 - 20%) и в общей сумме из 30% металлов, а 0 - 30% алюминия заменено пиролизом магния. Мы тоже исследовали и зависимость вязкости от состава и времени. Проведён и одновременный анализ интенсивности влияния перемены доли отдельных составляющих, а также и их совокупное воздействие на изменение вязкости с течением времени. Плотности образцов, взятых из различных сегментов зарядов взрывчатого вещества, определяются в соответствии со стандартом метода МИЛ 286Б, а затем определены и некоторые пористости.

Ключевые слова: **термобарические взрывчатые вещества, литые взрывчатые вещества, композитные взрывчатые вещества, АТС, перхлорат аммония, алюминий, магний, вязкость, плотность, пористость, перерабатываемость.**

Influence de la composition sur l'aptitude au traitement des explosifs thermobariques

Dans ce travail on a étudié l'influence de la composition des explosifs composites moulés thermobariques sur leur aptitude au traitement. Selon le plan expérimental 10 compositions différentes des explosifs thermobariques PBX ont été préparées par la technologie de la coulée. Les contenances des trois éléments étaient variées: liant thermodurcissable sur la base de polybutadiène hydroxyle terminé (15-20% en poids), ammonium perchlorate (0-20% en poids) et la participation de magnésium en quantité totale de 30% en poids du métal c'est-à-dire que 0-30 % en poids d'aluminium a été remplacé par le magnésium pyrolytique. La dépendance de la viscosité de la composition en temps a été examinée. On a analysé comment les changements de contenu des composantes individuelles affectent la dépendance viscosité6temps, séparément pour les trois composantes ainsi que leurs effets combinés. Les densités des échantillons prélevés dans les segments différents de charges explosives étaient déterminés selon la méthode du standard MIL 286B et les porosités étaient déterminées aussi.

Mots clés: **explosifs thermobariques, explosifs coulés, explosifs composites, PBX, ammonium perchlorate, aluminium, magnésium, viscosité, densité, porosité, aptitude au traitement.**