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ON SAFE COMBUSTIBILITY OF MIXTURES OF PROPELLANTS AND POLYMERS FOR MINES AND QUARRIES

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ABSTRACT
Mixtures of single-base propellant with chlorine and bromine-containing polymers in different ratios, applied in mines and quarries abroad, were investigated. The exo-effects: maximum temperature of the peak, quantity of released heat and loss of mass were determined by a differential scanning calorimetry, after a standard aging of 120 and 240 hours under conditions imitating the sunshine. Combustibility of mixtures was analyzed according to a standardized factor of combustibility (K), Mixtures were subdivided into four groups depending on their values: easily combustible, combustible, self-extinguishing and non-combustible. Effective action of selected compounds depended on speed of formation of combustion retardants, which depended on temperature of thermal destruction. That was the reason for mixing propellants with polymers, whose initial temperature of destruction had been lower than the temperature individual combustion of propellant. Thus effective combustion retardant was created in the initial stage of mixture heating.
Controllable fuel characteristics of recipes improve the safety of transport, storage and use of offered materials.

INTRODUCTION

Explosion transformation of propellant represents combustion with a maximum liberation of gas and minimum release of solid refuse. Propellant is continuously more often applied into mixtures with other explosives or additive as a new high-power source for mines and quarries. Raw material is easily achieved due to the excess and liberation from its main designation - in military arms and equipment.

Adding of polymers for regulating the combustibility of explosives is applied in different fields as pocket-building Kitano Y. (1997), pyrotechnics - Fire Retardant system(1996), processing of polymers - Wang Xu (1996).

Objective of the report, which is a continuation of the investigation of Ganev R., Glavchev I. (2002), is to characterize the safe combustibility of explosive mixtures of propellant and halogen-containing polymers, co-polymers and oligomers for mines and quarries.

EXPERIMENTAL

Subject of investigation are mixtures of single-base propellant (SBP) of Arsenal, Bulgaria with chlorine and bromine-containing polymers:

- Brominated epoxy oligomer (EOB),
- Vinyl chloride/Vinyl acetate (VC/VA),
- Epoxide oligomer of bisphenol (D600),
- Chlorinated rubber (CR),
- perchlorinevinyl (PCV),
- chlorinated paraffin (CP),
- mixed with the dillutors of acetone and cycloxexanone in the ratio of 1:1.

Mixture is coated over sheets of twice pickled steel of 120 x 90 mm size as films 20μm thick.

The factor of combustibility (K) is specified as a ratio of time for individual combustion of test samples to time for moving front of combustion to certain position of the test body Bulgarian State Standard SS 10457-(1998).

RESULTS AND DISCUSSION

Preliminary experiments revealed that not all the halogen-containing polymers posses the properties of effective additives for quarantining the safe combustibility of mixtures. Availability of enough chlorine and bromine is a required precondition. Bromine-containing epoxide compounds are more effective, and therefore the Br quantity in mixtures may be lower for achieving the required category of combustibility. Chlorine-containing polymers are less effective but cheaper and more widely applied.

The requirement for more effective action of Cl- or Br-containing polymers is determined by the speed of formation of combustion retardants, which depends on the temperature of polymer destruction. That was the reason for mixing single-base propellant SBP with polymers of initial temperature of destruction lower than the destruction temperature of single-base propellant SBP. Thus effective retardants of combustion are created in the beginning of heating.

Content of dry substance in the mixtures effects not only the mechanism and the speed of evaporation of solvents, but oalso on the kinetics of combustion transformation. Percent content of halogen and dry residue of mixtures of single-base propellant (SBP) with bromine and chlorine-containing polymers .is calculated. Mixtures consist of two or three components, and one of the pairs uses polyisocianate as a hardening agent. (table 1).

Table 1. Determination of the factor of combustibility K of coatings of coatings of single-base propellant SBP with polymers, co-polymers and oligomers

Test №	Composition of mixture	Ratio [%]	Dry substance [%]	Content of halogen [%]	Factor of combustibility **K**
1.1	SBP + EOB	80 : 20	13	Br 1,08	c o m b u s t i b l e
1.2		60 : 40	13	Br 2,16	self-extinguishing
1.3		40 : 60	13	Br 3,24	**high-flammability point**
2.1	SBP + EOB + hardener*	80 : 20	13	Br 1,06	c o m b u s t i b l e
2.2		60 : 40	13	Br 2,10	self-extinguishing
2.3		40 : 60	13	Br 3,12	self-extinguishing
2.4		20 : 80	13	Br 4,25	**high-flammability point**
3.1	SBP + EOB + D600	20 : 40 : 40	25	Br 4,16	self-extinguishing
4.1	SBP + D600 + CP	20 : 80 : 10	25	Cl 1,71	self-extinguishing
4.2		20 : 80 : 20	25	Cl 3,20	self-extinguishing
4.3		20 : 80 : 30	25	Cl 4,33	**high-flammability point**
5.1	SBP + D600 + PCV	20 : 80 : 12	25	Cl 1,96	self-extinguishing
5.2		20 : 80 : 18	25	Cl 2,78	**high-flammability point**
6.1	SBP + D600 + CR	20:80:20	25	Cl 1,67	self-extinguishing
6.2		20 : 80 : 40	25	Cl 2,87	**high-flammability point**

* The hardener used was toluene 2,4- diisocyanate (

Data in table 1 show that with the increase of halogen the concentration resistance against combustion rises also. Halogen-containing polymers decompose themselves and form halogens, halogen-hydrogen or halogen carbon-hydrogens, which expose their protecting effect in the gaseous phase mainly.

Due to the higher atomic mass of Br, the number of HBr molecules is lower than the number of HCl molecules for equal percent content of halogen. This explains the fact that comparatively low contents of halogen achieve a certain good effect, which is evidently shown for mixtures 1.2, 6.1 and 2.2, 5.1.

The other explanation is based on the structure of halogen-containing polymers or oligomers. Chlorine in the polymer is bound to a carbon atom of aliphatic molecule, while Bromine is bound to a carbon atom of aromatic core. It is known that the length of C-X bound in the first case is longer, therefore an atom Cl will easily separate and form HCl. On the contrary, the C-Br bound in EOB is shorter and atom of Bromine will separate with more difficulty as HBr, under same conditions.

Evaporation of solvent also effects on properties of spontaneous extinguishing – see mixtures 5.1 and 6.1 in the table. Evidently, the liberated quantity of solvents is higher for these mixtures. Data reveal that the combustibility of coating with lower content of halogen has a value analogous to the factor of combustibility K of coating, obtained from mixtures, characterized with lower speed of evaporation of solvents.

It might be suggested that type of combustibility of coating of single-base propellant SBP+polymer depends on the concentration, energy of tearing of X-X, H-X, C-X bonds, density of gases or vapours, temperature of evaporation and other less important factors. With the decrease of energy of binding in halogen-hydrogen, the density of vapours increases. This increases the concentration of non-combustible gases of the film surface, which starts in the initial stage of combustion and brings to reduction of the probability of firing.

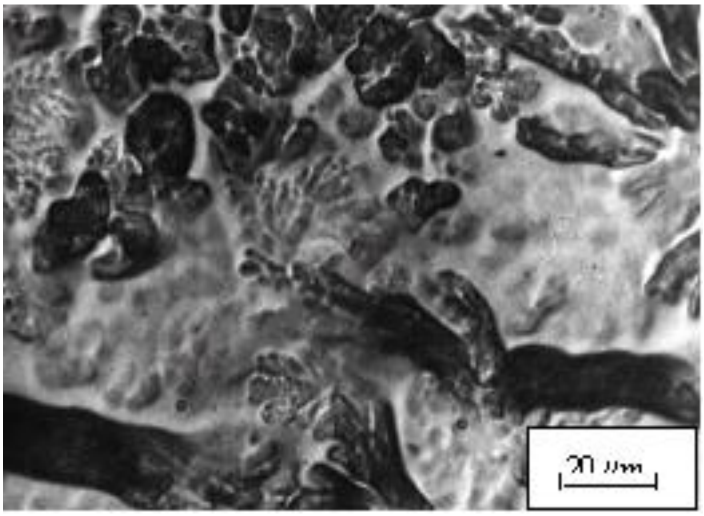
Inhibiting from active centres, able to form meshes in the beginning of destruction is possible. Other centres may impede the interaction between active radicals and macromolecules of pyroxiline or products of destruction, thus reducing the concentration of combustion gases. Meshing of coatings (mixtures 1.3 and 2.3) evidently makes difficult the evaporation of solvents, and this brings to reduction of the efficiency of selected polymers. For those mixtures, content of bromine is analogous, but mixture with hardening agent is spontaneously extinguishing, and without hardening agent is low combustible.

Results correlate to the data of Radhakrishnan G. (1992), but mixture of nitrocellulose with other polymers are used there. The above investigations are one more proof that polymers may be used to regulate the required safe combustibility of explosive compositions.

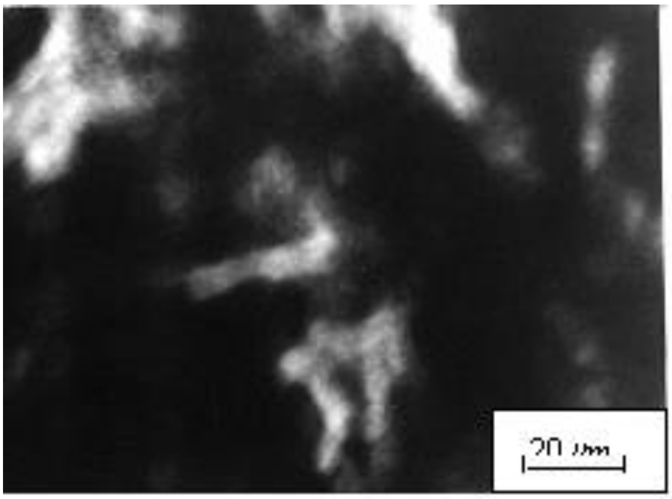
When single-base propellant SBP is mixed with a non-crystallizing polymer in a 1:1 ratio in CX as a solvent, even an amorphizing of films is not observed. (Fig. 1).

The microscopic photoes reveal the difference between over-molecule structures obtained from SBP+PCV (Fig.1a) and SBP+ПВХ (Fig.1б).

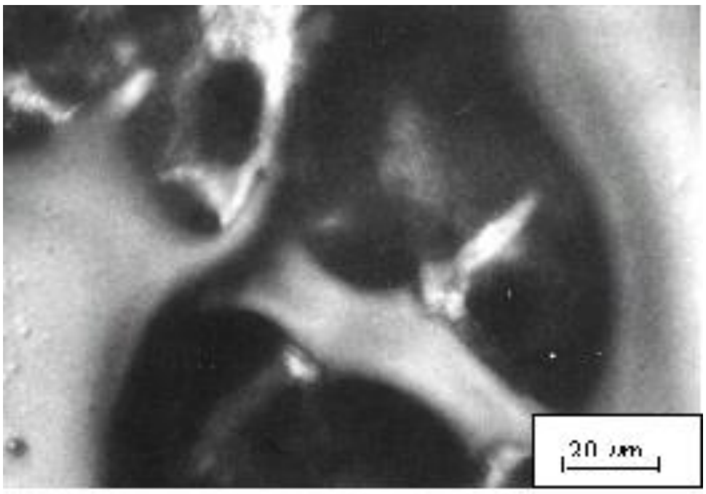
Over-molecule structures of 10 μm size are registered due to the amorphizing of film of single-base propellant under the action of PCV .For the mixture of SBP+PCB over-molecule formations are even heavilty amorphized.



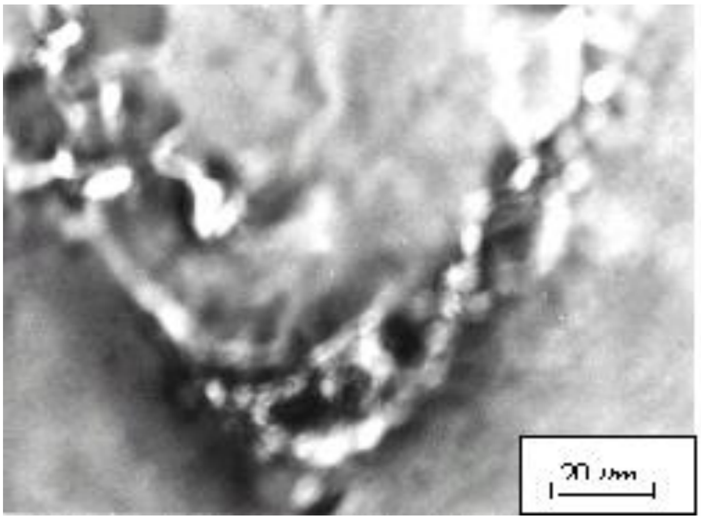
a) SBP+PCV $(\times 560)$



b*) (ЕЦ + PCV)* $(\times 560)$



c*) SBP + D600* $(\times 560)$



d) *SBP + PVB* $(\times 560)$

Figure 1. Microscopic photoes of films of the analyzed mixtures

Films of mixtures SBP+D600 (fig.1в) and SBP+PVB (fig.1г) have images of irregular shapes and show even an amorphizing of initial SBP. Amorphied fields surround the crystal structures. In those fields the macromolecules show increased movability, and crystal formations show lower volume.

There is no layering in the microscopic photoes, which is a proof for the thermodynamic compatibility of SBP with analyzed polymers, co-polymers and oligomers.

CONCLUSION

Analysis of results from determining the factor of combustibility K, from differential-scanning calorimetry and microscopic observations revealed that safe combustibility of explosive mixtures of propellant and polymers may be controlled effectively.

This conclusion proved the possibility for industrial modification of combustibility of produced single-base propellant for successful practical application into other non-military sectors, mine and quarries including. Improved safety of transport, storage and use will be a fact. The manufactured industrial product plastic or solid, depends on the requirements of technology, where it will be applied.

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