

New Series of Gas-Generating Compositions for Automobile Safety Bags

D. B. LEMPERT and G. B. MANELIS

*Institute of Problems of Chemical Physics, Russian Academy of Sciences,
Prospekt Akademika Semenova 1, Moscow Region, Chernogolovka 142432 (Russia)*

E-mail: Lempert@icp.ac.ru

Abstract

Modern requirements to smokeless gas generating compositions for automobile safety bags are described. Possible ways to decrease combustion temperature and the concentrations of toxic gases in combustion products are analyzed. Thermal stability of the potential components of gas-generating compositions (organic compounds) and the phase state of ammonium nitrate within the temperature range from -50 to $+100$ °C are investigated. The routes of phase stabilization of ammonium nitrate with organic compounds containing no metals or halogens are proposed. The regularities of combustion of the compositions are investigated, the ways of a substantial increase in the combustion rate of compositions based on ammonium nitrate are proposed.

Modern gunpowder for automobile safety bags should meet a broad set of strict requirements: smokeless combustion (that is, a composition should be based on CHNO compounds); high combustion rate and thermal stability, conservation of performance characteristics for 10–15 years, and the absence of toxic compounds (including nitrogen oxides and carbon monoxide) in combustion products.

The existing gas-generating (GG) compositions can be divided conventionally into three categories. The first one includes the systems in which metal salts are oxidizers (nitrates, azides, perchlorates *etc.*) [1–3]. The systems belonging to the second category contain ammonium nitrate (AN) as the oxidizer [4]. The compositions with azides have already been prohibited in the developed countries due to the toxicity of azides themselves; the presence of condensed combustion products is characteristic of the systems containing metals (mainly potassium salts). In order to prevent smoke or aerosol from getting into the passenger compartment, it is necessary to make filtration systems. The compositions with AN are free from this disadvantage, but AN has several phase transitions within the temperature range of performance (from -50 to $+110$ °C): V \rightarrow IV

at -17 °C, IV \rightarrow III at $+32.3$ °C, and III \rightarrow II at 84.2 °C [5–7]. Because of this, the structure of a composition containing AN gets destroyed when stored for a long time and under large temperature changes. On the other hand, the compositions with AN are characterized by very low combustion rate (about 3–5 mm/s at a pressure of 100 atm) [8, 9].

The third type of GG compositions includes stoichiometrically balanced mixtures of organic compounds (described by the general formula $C_aH_bN_kO_{2a+0.5b}$) one of which is an organic oxidizer based on a nitro or nitrate derivative. These systems are smokeless but their combustion temperatures are high (above 3000 K), so high concentrations of carbon monoxide and nitrogen oxides are present in combustion products. This is explained by the fact that at temperatures above 2400 K the equilibrium concentrations of these gases are very high; under a rapid expansion in the combustion chamber, the time is insufficient for the equilibrium to get established; the so-called quenching process occurs as a result.

The new gas-generating compositions devoid of the listed disadvantages should not contain any elements other than C, H, N and O; their composition should be close to the stoichiometric

one, but at the same time they should have low combustion temperature T_c (the desirable upper limit is 2000–2200 K) at which the equilibrium concentrations of CO and nitrogen oxides is negligibly small. In addition, they should be thermally stable because they may be heated to a high temperature during performance and get burnt down within 50–60 ms.

The development of GG compositions meeting all the formulated requirements is an extremely complicated problem because there are no organic compounds suitable for these purposes, solid and thermally stable; so, it is only possible to develop a stoichiometric mixture with $T_c < 2600$ K (at 100–200 atm) on the basis of AN.

Within the present work, we carried out thermodynamic analysis of the ways to make new organic compounds that would be able to become the basis of stoichiometric compositions with low T_c . The general dependencies of T_c on pressure, elemental composition and enthalpy of formation of a stoichiometric CHNO composition were determined [10]. Basing on the obtained analytical dependence, a user programme allowing one to arrange GG compositions with the required T_c from the available database of components was elaborated. It was shown that GG compositions with reduced T_c without AN may be possible only if they involve an organic compound in which one molecule includes both the conventional nitrogen- and oxygen-containing fragments ($-\text{NO}_2$, ONO_2 , $>\text{NNO}_2$) and low-enthalpy oxygen-containing fragments (ester, carbonyl, carboxylic, hydroxyl *etc.*) [11]. The compounds of this kind have not been previously investigated in the chemistry of organic nitrogen- and oxygen-containing oxidizers because it is impossible to use them as a basis for high-energy gunpowder, propellants and explosives. However, the problem of making ecologically safe GG compositions for automobile safety bags cannot be solved with the conventional oxidizers for gunpowder because for $T_c > 3000$ K the concentrations of hazardous NO and CO in the products of combustion of the stoichiometric compositions would be very high. A broad range of organic compounds was outlined which are to be synthesized and investigated. In part, these compounds have already been synthesized at

the Institute of Organic Chemistry (IOC), RAS, within the present work.

Second, experimental determination of thermal stability and compatibility of the investigated compounds was carried out; the possibilities to use a class of organic compounds as a component for GG compositions for automobile safety bags were analyzed, and the effect of functional groups on thermal stability was evaluated. Thermal stability requirements to the components of GG compositions for automobile safety bags are much more strict than even those to the components of gunpowder, explosives and propellants. The reason is that, unlike the latter that may be stored at the environmental temperature (that is, not higher than 45–50 °C), the sites where gas-generating inflators are situated in an automobile may have a temperature up to 100–110 °C. It was shown that many classes of conventional energetic compounds, for example organic nitroesters, do not meet the stability requirement. Polynitrocompounds, especially those based on aromatic cycles, are very stable, but when an additional low-entropy oxygen-containing (especially carboxylic) group is additionally introduced into a molecule in order to decrease combustion temperature, the stability of the resulting compound decreases sharply.

More than 30 new compounds of different classes were synthesized in the IOC, RAS, within the present investigation: derivatives of aliphatic carboxylic acids, carbamide, its linear and cyclic analogues, guanidine, hydroxylamine and some nitrogen-containing heterocycles, C-(2,2,2-trinitroethoxy) derivatives, 2,2,2-trinitroethyl esters of aromatic and heteroaromatic carboxylic acids. The majority of the synthesized compounds turned out to be insufficiently stable for use in automobile safety bags. Some of them, for example dinitroester of tartaric acid, slowly decompose even at room temperature; the level of stability of other compounds (for example, nitroguanidine nitrate) turned out to be 10–15 times lower than the required level [12]. There is a hope that these compounds will become suitable for safety bags if methods to stabilize them will be available (for example, by adding a stabilizing agent, such as diphenyl amine,

suppressing autocatalysts, or even by carrying out fine purification of a compound) or if the stability requirements are reduced. However, we discovered that some compounds meet or approach the stability requirements: these compounds incorporate $-\text{O}-\text{CH}_2-\text{C}(\text{NO}_2)_3$ and $-\text{C}(\text{O})-\text{O}-\text{CH}_2-\text{C}(\text{NO}_2)_3$ groups.

In addition, we investigated the problems of predicting the long-term storage of the compounds at increased temperatures and formulated the problem concerning selection of objective criteria for choosing the restrictions related to the admissible thermal stability level.

Third, we investigated the regularities of phase transitions in AN. In addition to investigating AN as an individual oxidizer, we studied also the product of its joint crystallization with potassium nitrate which eliminates phase transitions. It was shown that a solid solution in AN III phase can exist only with potassium nitrate concentration above 8 %; only in this case one can speak of irreversibility of the phase stabilization of AN. Though in the case when AN phase-stabilized with potassium nitrate is used as an oxidizer the fraction of the solid phase in combustion products is much lower in comparison with potassium salts and the salts of other metals, still the condensed phase is present in the products. Because of this, the main attention was paid to the search for the ways of phase stabilization with compounds containing no metals. It was discovered when investigating the kinetics of phase transformation in AN that the destruction of the initial phase along different directions in the crystal occurs not synchronously; so does the construction of the final phase. The limiting stage of the process is not the generation and growth of the centres of the new phase inside the initial one but the transition of the initial phase into some transition X-ray amorphous state which is further realized into a new phase. This is characteristic both for the direct and especially for the inverse transition. The inverse transition may even result in the formation of almost completely X-ray amorphous phase. It was shown that phase transitions are not characteristic of some products of the joint crystallization of AN with other salts or molecular compounds, as well as of some

substitutional solid solutions. For example, the product of the joint crystallization of AN with ammonium formate has not phase transitions within the temperature range from -50 to $+80$ °C. Stabilizing additives were found which inhibit the phase transition V-IV completely when added in small amounts to AN. In this situation, phase II gets transformed directly into phase IV omitting the formation of phase III, while phase transition IV-II proceeds at a temperature about 50 °C. Transformations IV-II destroy the mechanical structure of AN not so strongly as the transitions IV-III-II, which was demonstrated in multiple cycling changes of the sample temperature.

Fourth, the possibilities of a substantial increase in the rate of combustion of the compositions based on AN were investigated. Since the time of combustion of GG compositions for automobile safety bags should be very small (down to $50-60$ ms), the linear combustion rate should be about 25 mm/s at a pressure of 200 atm, that is, the combustion rate would be increased. Various new methods of the formation of fuel charge were successfully found, mainly due to the formation of porous compositions with definite porosity, which allows one to increase the combustion rate by a factor of several units and to govern its level.

CONCLUSIONS

As a result of investigations, possible ways to decrease the combustion temperature of stoichiometric compositions with the help of new organic oxidizers containing low-enthalpy oxygen-containing fragments in their molecules were proposed. New structures based on ammonium nitrate were found that do not exhibit phase transitions within the temperature range of performance, and stabilizers of phase transitions that decrease the number of phase transitions from 3 to 1 within temperature range from -50 to $+100$ °C, which provides the possibility to store the products under more rigidly variable temperature conditions. Thermal stability of a wide range of compounds – potential components of gas-generating compositions – was investigated and prediction of their behaviour during long-term storage

under elevated temperature was given; criteria for choosing the limitations concerning the admissible thermal stability level were elaborated. The regularities of combustion of stoichiometric gas-generating compositions based on ammonium nitrate were obtained; the methods of the formation of fuel charge by making porous compositions with definite porosity were found that allow one to increase several times the combustion rate.

Acknowledgement

The work was financially supported by the International Scientific and Technological Centre under Project No. 1882 "Development of non-toxic gas-generating compositions for automobile safety bags".

REFERENCES

- 1 Pat. 5861571 USA, 1999.
- 2 Pat. 5536340 USA, 1996.
- 3 Pat. 6113713 USA, 2000.
- 4 Pat. 6176950 USA, 2001.
- 5 M. J. Herrmann and W. Engel, *Propellants Explos.*, 22 (1997) 143.
- 6 S. Yamamoto and Y. Shinnaka, *J. Phys. Soc. Jpn.*, 37 (1974) 732.
- 7 B. W. Lucas, M. Ahtee, A. Hewat, *Acta Cryst. B.*, 35 (1979) 1038.
- 8 A. P. Glazkova, *Kataliz goreniya vzryvchatykh veshchestv*, Nauka, Moscow, 1976.
- 9 G. B. Manelis, G. M. Nazin, Yu. I. Rubtsov, V. A. Strunin, *Termicheskoye razlozheniye i gorenije vzryvchatykh veshchestv i porokhov*, Nauka, Moscow, 1996.
- 10 D. B. Lempert, G. B. Manelis, M. V. Makhonina, G. N. Nechiporenko, *Khim. Fiz.*, 22, 5 (2003) 65.
- 11 D. B. Lempert, G. N. Nechiporenko, G. B. Manelis *et al.*, *Termodinamicheskiye aspekty sozdaniya na baze CHNO-soyedineniy samogoryashchikh gazogeneriruyushchikh kompozitsiy s zadannoy temperaturoy gorenija*, *Materialy XIV Mezhdunar. konf. po khim. termodinamike*, St. Petersburg, 2002, p. 128.
- 12 G. B. Manelis, D. B. Lempert, G. N. Nazin, *Ways to Develop Gas Generating Compositions for Automotive Airbags*, *Proc. of Sino-Russia Seminar on New Progress in Energetic Materials*, China, Myannyang, Institute of Chemical Materials, 2004, pp. 319–331.