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Evaluation of malonanilides as new stabilizers for double-base propellants. (I)

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Abstract

Five malonanilide derivatives (M1–M5) were prepared by the reaction of ethyl malonate with aniline derivatives. These compounds were investigated as new stabilizers for double-base propellants (DBPs). The evaluation process has been performed through thermal stability tests, thermal analyses measurements (TGA and DSC) and kinetic parameters calculations (E_a). The results of the new stabilizers were compared with the results of the classical stabilizer *N,N*-diethyldiphenyl urea. It has been found that *o*- and *p*-dinitromalonanilides, in particular, showed better stability effect for DBPs than the classical one. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Stabilizers (malonanilides); Double-base propellants; Thermal analysis; Thermal stability tests

1. Introduction

Double-base propellant stabilizers are substances that can react with the products of decomposition of the propellants and remove them. They do not prevent decomposition, but they stop the catalytic action of the decomposition products such as NO, NO₂, HNO₂ and HNO₃. They stabilize the propellant by removing the products of decomposition as soon as formed and so the decomposition reaction being uncatalyzed and the propellant will have a much longer serviceable life.

Different classes of organic compounds like amines, amides, heterocyclic compounds which based on imidazole and pyrazole have been long recognized as stabilizers [1–6].

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The most important class of these compounds is the amines or those compounds contain the PhN moiety in their structure. One of the most commonly used classical stabilizer of this class is Centralite 1 (*N,N*-diethyldiphenyl urea).

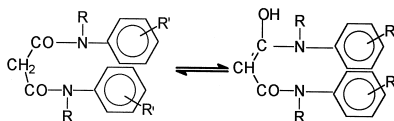
The evaluations of the double-base propellant stabilizers mainly depend on thermal stability tests [7]. In the last period of time, the thermal analysis techniques (TGA and DSC) were introduced as a second tool for evaluation of the double-base propellant stabilizers. The advantages of thermal analysis are the use of small samples and the short time to get reliable results. In this paper, thermal analysis is widely applied as a fast auxiliary method in the evaluation of the new stabilizers.

A number of malonanilide derivatives have been applied in studying dyes and pigments [8–10] pharmaceutical [11,12], stabilizers for polymers [13] and in thermal recording materials [14]. In this present work, we try to find a new application for some malonanilide derivatives (M1–M5) as stabilizers for double-base propellants.

The thermal stability tests, thermal analysis techniques (TGA and DSC) and the activation energy calculated by Ozawa method [15] were used to evaluate the new stabilizers.

2. Experimental

The chemicals used in preparation of malonanilides are diethylmalonate, aniline, *N*-ethylaniline, *o*-nitroaniline, *m*-nitroaniline and *p*-nitroaniline of purity 98% and produced by Merck and FIP companies. Malonanilides (M1–M5) were prepared by condensation reaction of diethylmalonate with aniline derivatives according to Chattaway method [16]. The propellant samples were prepared by a solventless process by mixing nitrocellulose (56%), nitroglycerin (27%), dinitrotoluene (9%), dibutylphthalate (4%), stabilizer (3%) and transformer oil (1%). Abel heat test at 80°C, Storage test at 100°C, Dutch heat test at 105°C, Bergmann–Junk test at 120°C, Calorific value and deflagration temperature measurement (Stability tests), were carried out according to the methods of Bofors [10]. For non-isothermal thermal and isothermal analysis (80°C, 105°C, 120°C, and 130°C), TGA and DSC of Shimadzu-50 were used to study the decomposition behaviour of propellant samples. All the thermal analysis experiments were carried out for 3–5 mg samples under inert nitrogen atmosphere with heating rate 5° min⁻¹.



M1 = malonanilide, R = H, R' = H.

M2 = *N,N'*-diethylmalonanilide, R = C₂H₅, R' = H.

M3 = *o,o'*-dinitromalonanilide, R = H, R' = *o*-NO₂.

M4 = *m,m'*-dinitromalonanilide, R = H, R' = *m*-NO₂.

M5 = *p,p'*-dinitromalonanilide, R = H, R' = *p*-NO₂.

3. Results and discussion

The evaluation of malonanilides (M1–M5) as a new stabilizers depends on a comparative study with the results of the classical stabilizers (diethyldiphenyl urea). The results of qualitative stability tests (Abel heat test and storage test) for the DBPs samples containing both new stabilizers and classical stabilizer show the same results (Table 1). The brown circle formed on the starch paper was formed after 45 min in case of Abel test and the brown fumes began to evolve after 12 days in case of storage test. The quantitative stability results (especially B & J) show that malonanilides divided into three groups according to their stabilizing effect in comparison with classical stabilizer. The first group includes *N,N'*-diethylmalonanilide and *o,o'*-dinitromalonanilide which have higher stabilizing effect (2.8 and 3.4 ml) than the classical one (4.0 ml). The second group includes *p,p'*-dinitromalonanilide, which nearly has the same stabilizing effect like the classical stabilizer. Finally, the third group of malonanilide derivatives (*m,m'*-dinitromalonanilide and malonanilide) has a lower stabilizing effect (4.9, 4.3 ml) than the classical stabilizer (Figs. 1–4).

The results of thermogravimetric analysis (TGA) under non-isothermal conditions show that in general, DTG peaks temperature of the propellant samples containing malonanilides (M2 = 205°C, M3 = 223°C, M4 = 210°C, M5 = 221°C) are higher than that of samples containing classical stabilizer (C1 = 203.4°C) (Table 2). Also, the time difference between starting decomposition and reaching the DTG peaks temperature is bigger in case of samples containing the new stabilizers (M1 = 8.21, M2 = 10, M3 = 14.7, M4 = 13.1 and M5 = 11 min) than that containing the classical one (C1 = 8.48 min). It was found that the stabilizer gave the propellant samples higher DTG peak temperature and longer time difference was *o,o'*-dinitromalonanilide (223°C and 14.7 min). The results of isothermal TGA at 80°C and 105°C show that the propellant samples containing malonanilides (M1 = 5.03%, 9.79%, M2 = 7.00%, 10.08%, M3 =

Table 1
Stability tests of malonanilides compared with classical stabilizer

Stabilizer	Abel heat test at 80°C (min)	Storage test at 100°C (days)	Dutch heat test at 105°C after				Bergmann –Junk test at 120°C (ml)	Calorific value (cal/g)	Deflagration temperature (5°C/min)
			8 h	24 h	48 h	72 h			
			Weight loss (%)						
C1	> 45	> 12	0.22	0.20	0.12	0.09	4.0	776	175
M1	> 45	> 12	0.25	0.17	0.13	0.10	4.3	–	–
M2	> 45	> 12	0.28	0.20	0.12	0.10	3.7	762	172
M3	> 45	> 12	0.26	0.22	0.16	0.10	2.8	784	172
M4	> 45	> 12	0.24	0.20	0.13	0.08	4.9	–	–
M5	> 45	> 12	0.23	0.21	0.13	0.07	4.1	776	170

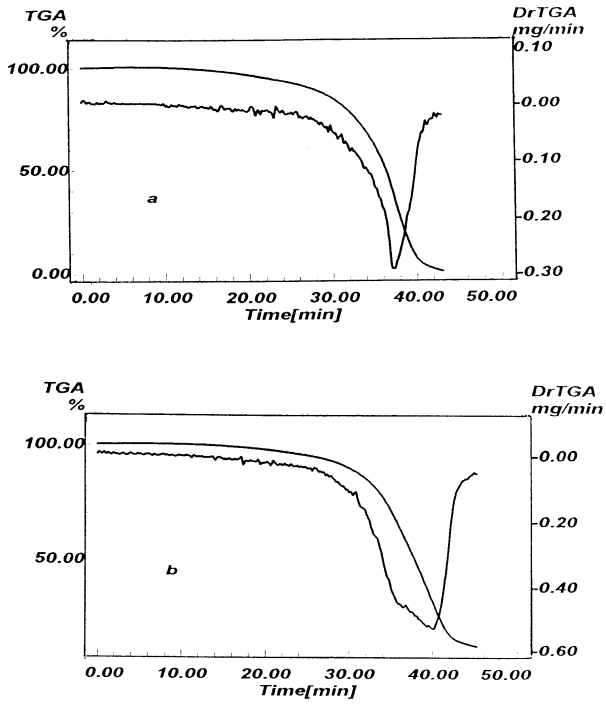


Fig. 1. C1 and M3.

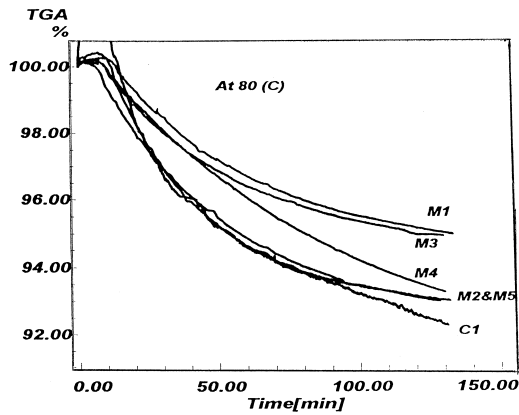


Fig. 2. C1, M1–M5.

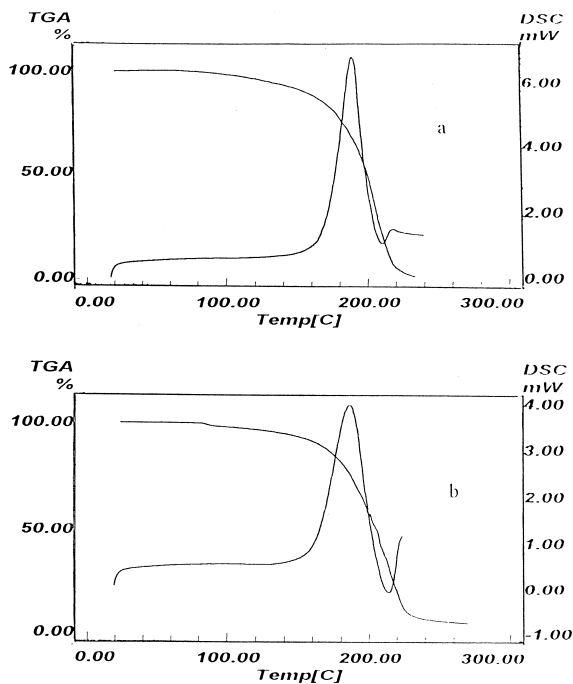


Fig. 3. C1 and M1.

5.09%, 8.26%, M4 = 6.73%, 10.42% and M5 = 7.02%, 12.54%) have lower weight loss percentages than the propellant sample containing the classical stabilizer (C1 = 7.74%, 11.42%) as given in Table 3. At 120°C, the malonanilides divided into two groups according to their stabilizing effects in comparison with the classical stabilizer. The first group includes *N,N'*-diethylmalonanilide and *p,p'*-dinitromalonanilide which is given the propellant samples lower stabilizing action (M2 = 20.79% and M5 = 21.2%) than the classical one (C1 = 19.63%). The second group includes the other malonanilide derivatives under investigation which gives the propellant samples higher stabilizing action in comparison with the classical stabilizer. The situation changes completely at 130°C, with the propellant samples containing the classical stabilizer having the lowest weight loss (22.16%) among the different stabilizers. The above results showed that the new stabilizers (malonanilides) in general give the double-base propellant higher stabilizing action than the classical stabilizer.

The results of TGA of different propellant samples within the decomposition range (DSC results) are given in Table 4. The propellant sample containing *o,o'*-dinitromalonanilide lost 45.9% of its weight within the decomposition range (151.1–209.3°C). This is the best value among the different stabilizers including the classical stabilizer. In the other case, the propellant sample containing *m,m'*-dinitromalonanilide lost 85% of its weight within its decomposition range (156.5–227.3°C). This is the worst value between the different stabilizer under investigations. Between the above two values, the results of the other stabilizer under evaluation have been obtained. These

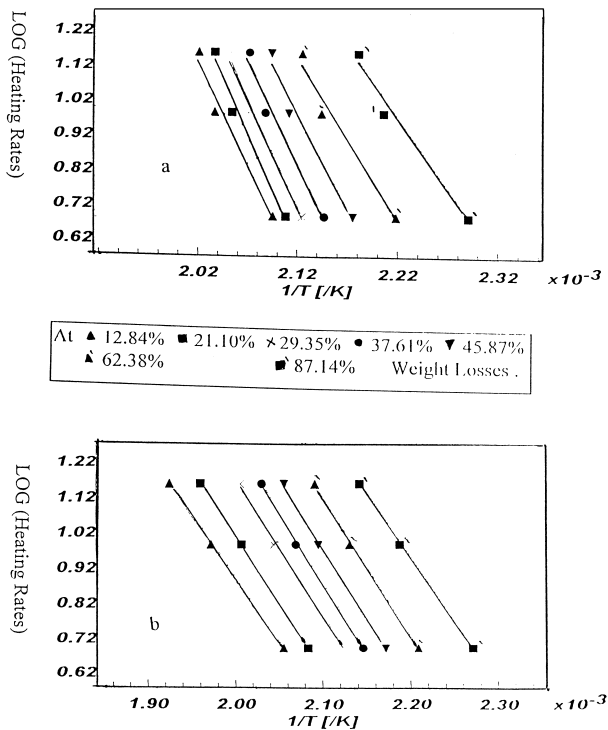


Fig. 4. C1 and M1.

results assured that malonanilides could be considered as new stabilizers for double-base propellants.

The results of kinetic parameter calculated by Ozawa method are given in Table 5. *o,o'*-Dinitromalonanilide gave the propellant sample the highest activation energy (143.43 kJ mol⁻¹), and the stabilizer malonanilide gave the propellant sample the lowest

Table 2

Decomposition temperatures of propellant samples containing different stabilizers

Stabilizers	Temperature of starting decomposition (°C)	DTG peak temperature (°C)	Rate of maximum weight loss (mg/min)	Time difference between starting decomposition and DTG peak temperature (min)
C1	153.3	203.4	0.29	8.48
M1	153.3	201.6	0.39	8.21
M2	153	205	0.36	10
M3	151.5	223	0.53	14.7
M4	155.8	210	0.39	13.1
M5	156	221	0.49	11

Table 3

Isothermal TGA of the propellant samples containing different stabilizers at different fixed temperatures (80°C, 105°C, 120°C, and 130°C)

Added stabilizers	Isothermal temperatures (°C)			
	80	105	120	130
	Weight loss (%)			
C1	7.74	11.42	19.63	22.16
M1	5.03	9.79	16.92	27.94
M2	7.00	10.8	20.79	32.07
M3	5.09	8.26	13.3	23.43
M4	6.73	10.42	15.65	37.08
M5	7.02	12.54	21.2	24.58

Table 4

DSC results of propellant samples containing different stabilizers with correlation of TG losses within the decomposition range ($T_i - T_f$)

T_i = temperature of starting decomposition, T_m = peak temperature, T_f = temperature of ending decomposition.

Stabilizers	T_i	T_m	T_f	Percentage weight losses (%)
C1	162	189.1	210.7	80.8
M1	159	186.8	213.2	72.5
M2	160.2	191.7	210.9	65
M3	151.1	189.8	209.3	45.9
M4	156.5	188.2	227.3	85
M5	155.6	190.4	210.7	48.3

Table 5

Kinetic parameters of the thermal decomposition of propellant samples containing different stabilizers from non-isothermal TGA

Added stabilizers	Activation energy (kJ mol^{-1})	Frequency factor (min^{-1})	Order
C1	93.11	1.03×10^{10}	0.8
M1	70.72	5.64×10^6	0.6
M2	109.6	1.96×10^{11}	0.7
M3	143.43	1.48×10^{15}	1.5
M4	80.64	5.83×10^7	0
M5	139.31	2.26×10^{14}	1.2

activation energy ($70.72 \text{ kJ mol}^{-1}$). The values of the activation energies of the propellant samples containing the other stabilizer came between the above two values.

4. Conclusions

1. The thermal analysis techniques can be considered as auxiliary tool in evaluation of new stabilizers for double-base propellants.
2. Malonanilides can be considered as good stabilizers for double-base propellants.
3. *o,o'*-Dinitromalonanilide is considered as the best stabilizer between the different malonanilide derivatives (M1–M5).

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