Pyrotechnic mixtures based on anthracene for generation of carbonaceous aerodispersion attenuating infrared radiation

by Ladislav KLUSÁČEK* and Petr NAVRÁTIL*

It was proved experimentally that aerodispersions generated from pyrotechnic mixtures on the basis of anthracene containing a high portion of carbonaceous particles can efficiently attenuate infrared (IR) radiation. Under variable field conditions smoke cartridges with optimised mixture generated clouds of aerodispesions and the mean IR attenuation values were $L_{(3\text{-}5)} = 14.2+2.0$ dB and $L_{(10.6)} = 6.1+0.4$ dB. Attenuation values in mid-IR radiation region (λ = 3-5 μm) met the requirement, being close to their half-values in far region of IR radiation.

The DM-11 small smoke cartridge introduced into service hitherto with the mixture based on ammonium chloride (Jershev mixture) generated aerodispersion not providing efficient protection in IR radiation region.

1. Introduction

Atmosphere is transparent for electromagnetic radiation of visible region (0.4 − 0.7 μm), near infrared region (0.7 − 1.1 μm), mid-infrared region (3-5 μm) and far infrared region (8-14 μm) which needs to be attenuated in present military practice. Military uses these radiations[1] for the operations of sophisticated reconnaissance and reconnaissance-firing weapons systems and in high-precision guided weapons. Carbonaceous aerodispersions can attenuate this radiation and can camouflage target[2] because carbon particles are highly absorbing at visible and IR regions[3]. They are one of the measures of complex camouflage providing an efficient protection of own units, equipments and devices against the above mentioned weapons systems and means of reconnaissance.

Though many smoke-generating agents are known for heaving been used for generation of camouflage smokes as a protection against visual reconnaissance, new agents are examined and developed enabling screening also in the region of infrared radiation against sophisticated reconnaissance and firing systems.

Potential agents seem to be those ones creating carbonaceous aerodispersions in the course of pyrotechnic burning.

2. Theoretical Part

2.1 Optical properties of carbonaceous aerodispersions

Burning of quantitatively new hexachloroethane mixtures resulted in generation of high portion of carbon (20-36 %) with the except of products with magnesium and chloride ions. In IR region of spectrum there was measured[4] 40-times higher camouflage ability of their aerodispersions than in smoke generated from a standard mixture. This was explained by combination of the absorption effect of radiation at the wavelength of 3-12 μm (approx. 25 % portion of the total effect) and dispersion effect on relatively big carbonaceous particles. These pieces of knowledge about attenuation abilities of carbon towards radiation resulted in its more detailed study. Crystallinite carbon blacks and graphite were examined as possible camouflage agents[5]; measurements were carried out with pellets of carbonaceous agents and potassium bromide. Size of carbon blacks being usually spherical and polydispersive in pellets varied, most often, within 2-3 μm, and size of graphite particles was in the order of 10 μm. Carbon blacks were

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*Vojenský technický ústav ochrany (The Military Technical Institute of Protection)
POB 547, 602 00 Brno, Czech Republic
TEL +42-05-4118 3638

of long chain form and displayed higher camouflage abilities at the wavelengths of about 10 μm than spherical particles [6].

With regard to the above mentioned pieces of knowledge carbonaceous aerodispersions seemed to be more promissing for camouflage usage in IR region of radiation.

2.2 Pyrotechnic mixtures

Carbonaceous aerodispersions can be created from pyrotechnic mixtures of smoke-generating means of suitable composition by their pyrotechnic burning. From pyrotechnic mixtures, for utilization there can be considered, for example that ones containing high-boiling hydrocarbons [6].

Pyrotechnic mixtures of this character were based on aliphatic and preferably aromatic hydrocarbons with high boiling points (naphtalene, anthracene) which resulted in priority development of carbonaceous aerosol. Aerodispersions represented typical black smoke [7] are characteristic of high portion of carbonaceous particles. Mixtures were designed for signaling smoke means generating black smoke, composition of this simplest smoke-generating pyrotechnic mixture consisted of oxidising agent potassium perchlorate (55.0 %) and propellant (smoke generating agent, in the same time) anthracene (45.0 %). Burning of the mixture can be represented by the following possible reaction scheme (it was estimated that there was 66 % of solid particles in aerodispersion generated from this pyrotechnic mixture):

$$4KClO_4 + 2C_{14}H_{10} \rightarrow 4KCl + 10H_2O + 3CO_2 + 25C$$

Composition of this kind of pyrotechnic mixtures with anthracene or naphtalene for signal smokes was often modified.

In our laboratory there were studied attenuating characteristics of carbonaceous aerodispersions of smoke cartridges made on the basis of typical anthracene mixture with the purpose of potential application in camouflage in the region of IR radiation. They were compared with aerodispersions of introduced into service DM-11 smoke cartridges filled with modified Jershev mixture [9, 10] in the field conditions. Ammonium chloride was used in it as the smoke generating agent itself (for visible region of radiation). It was partly dissociated to gaseous products due to temperature of burning which again associated to aerosol particles of ammonium chloride after being cooled.

Reaction of the components in pyrotechnic mixture in the course of this mixture burning, where anthracene is mostly propellant, can be represented in the following possible way:

$$7KClO_3 + 2C_{14}H_{10} + 26NH_4Cl \rightarrow 7KCl + 8CO_2 + 5H_2O + C_{14}H_{10} + 6C + 26NH_4Cl$$

It is estimated that there are solid and liquid products of this reaction of 83 % from which only a small part (almost 3 %) belongs to carbon. High attenuation abilities of this aerodispersion against IR radiation cannot be, therefore, expected.

3. Experimental Part

3.1 Instruments

The following instruments and equipments were used in the course of field tests:

Diode Transmittometer with detector and source located in front of the object of observation. Wavelength $\lambda_{(1)} = 0.82$ μm.

Transmittometer with HgCdTe detector and IR source located in front of the object of observation. Wavelength $\lambda_{(2)} = 3\text{-}5$ μm.

CO_2 Laser Transmittometer. Wavelength $\lambda_{(3)} = 10.6$ μm.

PC Computer 286 with PCL 812 Card, ALEF, GOLD STAR Monitor, Thailand. TURBOPASCAL programme language, own modification.

AHLBORN -THERM 2280-8 Meter with NiCr-Ni(K) thermocouple measuring sensor. AHLBORN, Mess- und Regelungstechnik, Holzkirchem, FRG.

3.2 Smoke-generating means

The DC small smoke cartridge (black) of own construction, mass of the charge based on anthracene is 1000 g. Electrical initiator EPIO. The DM -11 smoke cartridge, mass of the charge on chlorideanthracene base is 1200 g. Heat percussion cap. Former ČSSR provenience.

3.3 Methods of measurement

In the course of field measurements groups of 5 pieces of smoke means were ignited. They were laid in chess-like arrangement in two rows between the object camouflaged and measuring instruments (3pcs/2pcs) so as to have distance of 4 m between

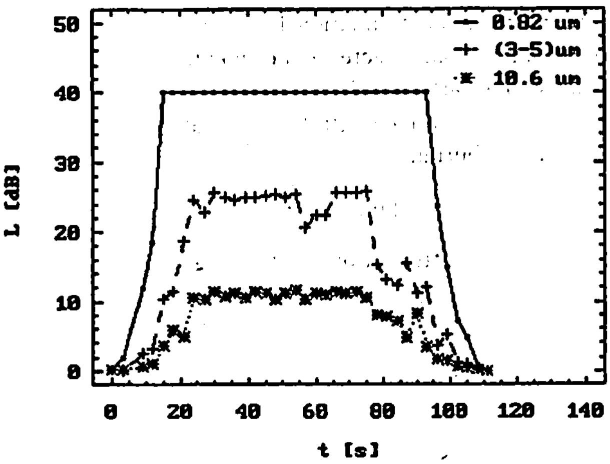

Fig. 1 Time changes of radiation attenuation L caused by aerodispersion developed from 5 pieces of DC smoke cartridges (experiment 4.10.)

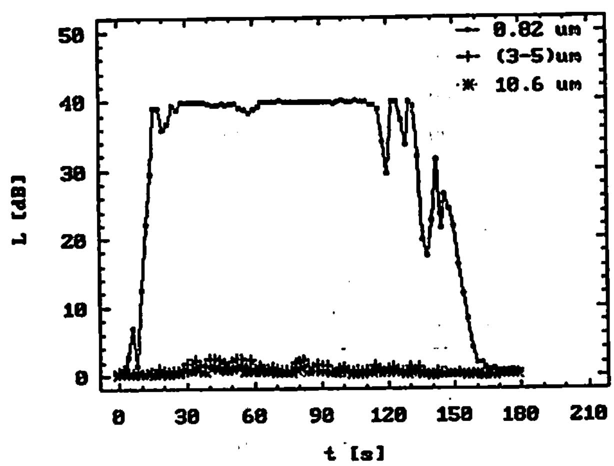

Fig. 2 Time changes of radiation attenuation L caused by aerodispersion developed from 5 pieces of DM-11 smoke cartridges (experiment 37.9.)

the individual means.

Particle concentrations of the aerodispersions measured were determined from the estimates of aerodispersion cloud dimensions both from the front and side video records and from the burning off of mixture mass with time.

4. Results and Discussion

It can be judged from the theoretical part analysis that mixture, containing high-boiling hydrocarbons like anthracene, generate aerodispersion with high portion of component with carbon. This can be a significant agent attenuating IR radiation.

Based on laboratory experiments there were made smoke cartridges with optimised pyrotechnic mixtures on the anthracene basis with combustion products flow from smoke cartridge which were, in the course of field measurements, also tested from the viewpoint of attenuation abilities of the aerodispersions generated. Wind was blowing perpendicularly to the direction of radiation transmit and measured in 75 % of experiments which represented last favourable conditions for the object camouflage.

Table 1 Mean calculated values of 0.82 μm radiation attenuation $\overline{L}_{(0.82)}$ caused by aerodispersions taken from 4-7 experiments made with 5 pieces of smoke means under various meteorological conditions

Smoke means	$\overline{L}_{(0.82)}$ [dB]
DM-11	35.9 ± 0.9
DC	39.5 ± 0.2

Smokes generated from these means were compared with aerodispersions of the introduced into service DM-11 smoke cartridge in which ammonium and potassium chloride were the camouflaging agents.

There were determined values of mean attenuation in the individual measurements taken from measured partial values of attenuation in time intervals in the course of pyrotechnic mixture burning. Time of mixture burning should be understood as period of time between the time of getting to burn and time of finishing to burn characterised by the highest, and for simplification sake, constant maximum radiation attenuation of smoke generated. Examples taken from the individual experiments for DC and DM-11 smoke cartridges are on Figures 1 and 2 exhibiting development the radiation attenuation by the aerodispersions changed with time.

In all the experiments implemented there were used groups of 5 pieces of smoke cartridges located in chess-like arrangement in front of the object screened. Aerodispersions from all kinds of smoke means attenuated perfectly visible radiation and radiation in near IR region at 0.82 μm. This is evidenced by Table 1 in which mean calculated values of the attenuation measured (with the experimental standard deviation of the mean[11,12] $S_x = \pm s / \sqrt{n}$, where s is the experimental standard deviation) are stated from n = 4-7 experiments with individual smoke means measured.

Mean values of radiation attenuation caused by aerodispersions of the means tested at 0.82 μm are high. This gives evidence of perfect attenuation of

Table 2 Mean values of 3-5 μm and 10.6 μm radiation attenuation $\overline{L}_{(3\text{-}5)}$ and $\overline{L}_{(10.6)}$ caused by aerodispersions taken from selected experiments made with 5 pieces of DC (black) smoke cartridges in chess-like arrangement, and times of attenuation 3-5 μm wavelength $t_{\mathrm{ů}(3\text{-}5)}$ and at 10.6 μm wavelength $t_{\mathrm{ů}(10.6)}$, and time of burning t_h

Experiment number	Mean values measured				Time [s] of		
	$\overline{L}_{(10.6)}$ [dB]	n	$\overline{L}_{(3\text{-}5)}$ [dB]	n	attenuation $t_{\mathrm{ů}(10.6)}$	$t_{\mathrm{ů}(3\text{-}5)}$	burning t_h
4.5	7.0	24	–	–	75	–	–
11.5	8.0	32	–	–	120	–	–
22.5	5.7	18	–	–	95	–	–
31.5	6.6	14	–	–	80	–	–
48.5	5.0	28	–	–	145	–	–
57.5	5.3	19	–	–	90	–	–
6.6	4.0	29	–	–	105	–	–
14.6	6.9	19	–	–	60	–	–
21.6	6.8	22	–	–	75	–	–
15.7	5.6	25	–	–	50	–	95
23.7	5.8	26	17.1	7	80	110	95
27.7	5.4	33	6.9	7	90	35	120
43.7	5.7	31	–	–	75	–	100
56.7	5.7	22	–	–	85	–	95
8.8	–	–	18.7	18	–	83	–
21.8	–	–	12.6	18	–	102	–
4.9	5.1	12	9.2	12	103	91	115
19.9	3.9	11	11.2	12	75	74	104
4.10	11.0	18	24.2	19	79	90	95
Mean	6.1		14.4		87	84	102
$\pm s/\sqrt{n}$	0.4		2.1		5	9	3

radiation by aerodispersions (maximum attainable value of attenuation with detector used was 40.0 dB) from both types of smoke means. Lower values of DM -11 attenuation stated in Table 1 included more substantial influence of changeable wind on local changes of aerodispersion concentration in the cloud developed. This was manifested in fluctuation of local concentrations in the cloud on the optical ray trajectory[13].

Mean values of radiation attenuation by means of aerodispersions in middle and far region of IR radiation calculated from measured data of time development of individual experiments enabled to evaluate camouflage abilities of pyrotechnic mixtures of smoke means for the demands of military utilization sufficiently trustworthy. It is evident from Table 2 in which the results of field measurements with optimised mixture based on anthracene are summarised (n is a number of value data of attenuation in the course of development of individual experiments with time, i.e. after corresponding time of attenuation $t_{\mathrm{ů}}(\lambda)$ the mean value was calculated from).

From the results in Table 2 follows that aerodispersion with preferential development of carbon attenuated perfectly in mid-region of IR radiation of 3-5 μm. Mean value $\overline{L}_{(3\text{-}5)} = 14.4+2.1$ dB containing changeability of weather conditions is getting very close to the value required (i.e. 15 dB). Mean attenuation $\overline{L}_{(10.6)} = 6.1+0.4$ dB meets the requirements from 40 %. Approximately the same times of the attenuations stated for the both regions of IR radiation $t_{\mathrm{ů}(10.6)} = 87$ s and $t_{\mathrm{ů}(3\text{-}5)} = 84$ s) were provided with average time of burning of DC smoke cartridge $t_h = 102$ s.

Comparison of similar data from the experiments with the present introduced DM-11 smoke cartridges

Table 3. Mean values of 3-5 μm and 10.6 μm radiation attenuation $\bar{L}_{(3\text{-}5)}$ and $\bar{L}_{(10.6)}$ caused by aerodispersions taken from selected experiments made with 5 pieces of DM -11 smoke cartridges in chess-like arrangement, and times of attenuation 3-5 μm wavelength $t_{\text{ü}(3\text{-}5)}$ and at 10.6 μm wavelength $t_{\text{ü}(10.6)}$, and time of burning t_h

Experiment number	Mean values measured				Time [s] of		
	$\bar{L}_{(10.6)}$ [dB]	n	$\bar{L}_{(3\text{-}5)}$ [dB]	n	attenuation $t_{\text{ü}(10.6)}$	attenuation $t_{\text{ü}(3\text{-}5)}$	burning t_h
29.5	3.0	95	–	–	340	–	–
46.5	2.0	82	–	–	400	–	–
55.5	1.4	91	–	–	350	–	–
5.6	5.2	114	–	–	320	–	–
30.6	4.7	110	–	–	310	–	–
37.7	1.4	105	–	–	320	–	400
41.7	1.9	109	–	–	320	–	420
54.7	1.8	136	–	–	410	–	520
17.8	–	–	4.2	23	–	480	–
2.9	0.5	20	1.0	20	300	320	420
37.9	0.7	62	4.3	40	105	120	130
6.10	–	–	2.0	30	–	320	–
20.10	1.5	17	–	–	300	–	340
Mean	2.2		2.9		316	310	372
$\pm s/\sqrt{n}$	0.4		0.7		23	39	49

indicates advantages of the DC smoke cartridge which can be confronted with data from Table 3. Also these data were obtained in the course of measurement taking place under different year and day meteorological conditions.

Mean attenuation values of IR radiation of the wavelength of 10.6 μm make $\bar{L}_{(10.6)} = 2.2$ dB for aerodispersions generated from the DM-11 under changeable meteorological conditions. Compared with the attenuation values of carbonaceous aerodispersions generated from the DC smoke cartridge these are the values three times lower. Mean attenuation values of radiation of the wavelength of 3-5 μm are $\bar{L}_{(3\text{-}5)} = 2.9$ dB compared with aerodispersions generated from the DC cartridge $\bar{L}_{(3\text{-}5)} = 14.4$ dB which is, thus, five times lower. Camouflage abilities of carbonaceous aerodispersions generated from the DC smoke cartridges in the regions of spectra stated are, thus, more effective.

Time development of radiation attenuation of aerodispersions in near IR region at 0.82 μm, i. e. in the course of attenuation time $t_{\text{ü}}$, as can be seen in Graphs 1 and 2, can be stated identical with burning time of the means. Attenuation times of carbonaceous aerodispersions in IR region at the wavelength 3-5 μm and 10.6 μm are, however, shorter which can be proved by Tables 2 and 3. This is, most propably, caused by more retarded generation of sufficiently high concentration of aerodispersion in the cloud being able to attenuate radiation effectively in longer wavelengths which was reached by burning of pyrotechnic mixture. During the experiments there were no substantial differences in attenuation times $t_{\text{ü}}$ between carbonaceous aerodispersions generated from the DC and from the DM-11 smoke cartridges at the both wavelengths 3-5 μm and 10.6 μm.

5. Conclusion

The following conclusion can be formulated from the work submitted:

1. Carbonaceous aerodispersions were indicated as efficient for IR radiation attenuation within the whole spectral width. The experiments carried out with selected pyrotechnic mixtures in smoke means generating aerodispersions of this kind proved this fact. Carbonaceous aerodispersions can be created by suitably constructed pyrotechnic mixtures the

base of which is preferably anthracene as a representative of high-boiling hydrocarbons. Carbon portion in the combustion products from the mixture modified containing ammonium chloride as a smoke-generating agent with anthracene as a propellant is lower which also predeterminates lower camouflage abilities of the aerodispersion generated. However, these last mentioned pyrotechnic mixtures cannot be excluded from possible utilization in such a case when pyrotechnic burning will result in generation of combustion products with more considerable carbon portion due to their suitably chosen composition of components in the pyrotechnic mixture.

2. Field experiments carried out under variable weather conditions with optimised pyrotechnic mixture based on anthracene in the DC means with smoke-cartridge flow of combustion products proved their high efficiency in radiation attenuation by carbonaceous aerodispersions in the mid-region of IR radiation. Mean attenuation value under the conditions stated made $\overline{L}_{(3\text{-}5)} = 14.4+2.1$ dB. Mean attenuation value of radiation in far IR region was $\overline{L}_{(10.6)} = 6.1+0.4$ dB. The values of attenuation reached the values required in the first case, in the second case they were close to the half of the values required.
3. Smoke means introduced into the Czech Republic Army till now as the DM-11 smoke cartridge do not provide efficient protection against radiation of IR spectrum. Mean attenuation value of radiation of 10.6 μm wavelength measured at aerodispersions generated from the DM-11 was $\overline{L}_{(10.6)} = 2.2$ dB under variable meteorological conditions. Mean attenuation value of radiation of 3-5 μm wavelength was $\overline{L}_{(3\text{-}5)} = 2.9$ dB.
4. The DC smoke cartridges with utilised smoke pyrotechnic mixture based on anthracene and smoke-cartridge like arrangement of combustion products discharge with mean burning time of pyrotechnic mixture $t_h = 102+3$ s generated carbonaceous aerodispersion of mean concentration in the cloud $c = 260$ mg.m^{-3}. Mean attenuation values for this smoke means were determinated after attenuation time $t_{ú(3\text{-}5)}$ and $t_{ú(10.6)}$ which reached approximately 80 % of mean burning time t_h. Similar portions of the both attenuation times were observed at aerodispersions generated from the DM-11 smoke cartridge. However, their mean attenuation values at individual wavelengths of IR radiation were low.

Literature

1) L. Klusáček, "Screening Aerosols as Prospect Field in Army" (in Czech). In: Sborník VÚ 070 Brno č. 2, 37 (1990).
2) A. Singh, S.G. Avachat, H. Singh, J. Sci. and Ind. Research 53, 667 (1994).
3) P. Chylek, V. Ramaswamy, R. Cheng, R.G. Pinnick, Appl. Opt. 20, 2980 (1981).
4) J.T. Hanley, J.N. Kile, B.J. Wattle, E. Mack, "IR and Visible Wavelength Obscuration for Pyrotechnically Generated Alkali Halide Smokes. "Rep. No. 7031-M-1. Arvin Calspan, Advanced Technology Center, Buffalo 1983.
5) J. Pinto, D. Wiegand, "Experimental Studies of the Optical Extinction of Various Forms of Carbon." In: R.H. Kohl, (Ed.): Proceedings of the 1979 Chemical Systems Laboratory Scientific Conference on Obscuration and Aerosol Research. Rep. No. ARCSL-CR-81023. Ronald H. Kohl and Ass., Tullahoma 1980. P. 375-386.
6) L. Klusáček, "Aerosols for Screening Purposes". Research Report (in Czech). VÚ 070, Brno 1985. OR-41/86-T.
7) J.H. McLain, "Pyrotechnics." The Franklin Inst. Press, Phyladelphia 1980. P. 63-79.
8) L. Klusáček, P. Navrátil, "Pyrotechnic Compositions for Developmment of Carbonaceous Aerodispersions Attenuating Infrared Radiation" (in Czech). In: Sborník VTÚO Brno No. 1, (1996), in press.
9) A.A. Shidlovskij, "Bases of Pyrotechnics" (in Czech). NV, Praha 1957. P. 230-243.
10) P. Prjashka, Vojennyj vestnik No. 1, 86 (1987).
11) V. Pechoč, "Evaluation of Measurements and Calculation Methods in Chemical Engineering" (in Czech). SNTL, Praha 1961. P. 18-25.
12) International Vocabulary of Basic and General Terms in Metrology. 2nd Ed. International Organization for Standardization 1993. P. 25.
13) E. Stryszak, "Visibility of Objects Observed through the Moved Gaps of Aerosols" (in Polisch). In: Biuletyn Wojskowej ekademii technicznej 34, No.3, 91-105 (1985).

赤外線減衰効果を用いた炭素エーロゾル生成用のアントラセン基剤火工品組成物

Ladislav KLUSÁČEK*, Petr NAVRÁTIL*

アントラセンを基剤とする火工品組成物から発生するエーロゾルは，炭素粒子の濃度が高く，赤外線の減衰効果があることが実験的に明らかとなった。エーロゾル生成のための最適混合のスモークカートリッジは各種の実際的な条件下でエーロゾルを形成し，平均の赤外線の減衰値は$L_{(3-5)}=14.2+2.0$ dBと$L_{(10.6)}=6.1+0.4$ dBとなった。赤外領域（$\lambda=3\sim5\,\mu m$）での減衰値は規定値となったが，遠赤外領域では規定値の半分の値であった。

現在使用されている塩化アンモニウムを基剤とする（Jershev混合物）エーロゾル発生用小型発煙カートリッジ，DM-11には赤外線減衰効果はなかった。

(*The Military Technical Institute of Protection, POB 547, 602 00 Brno, Czech Republic)