Analyses of New Nontoxic Stabilizers and Other Components in Smokeless Powders

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Abstract: Propellants consisting of nitrocellulose and/or other nitric esters are inherently chemically unstable and undergo decomposition even under standard storage conditions. Decomposition of such compounds can be inhibited or nearly stopped when stabilizers are used. However, conventional stabilizers form nitrosamines that have toxic and carcinogenic effects. A nitrocellulose based propellants contained new nontoxic stabilizers were prepared on this account. The new stabilizers are epoxidized oils (soybean oil, linseed oil and mixture fatty acids, C14-22). The chemical structure of the new stabilizers and their decomposition products should prevent the formation of toxic N-nitrosamines. We prepared double base propellants and these powders were investigated using Microcalorimetry, Conventional Stability Tests and Sensitivity Tests. The results were compared with propellants containing the conventional stabilizer akardite II. Qualitative and quantitative analyses were also performed. These analyses are very important next to the Conventional Stability Tests and Sensitivity Tests. Therefore, this paper presents qualitative and quantitative analyses results of the new substances as stabilizers for propellants. We studied options of oils stabilizers determination and mechanism of stabilization of propellants by oils. Paper describes quantitative analyses results of other substances in propellants (nitroglycerin and solvents) too and options of samples modification before analyses.

Keywords: smokeless powders, chemical stabilizers, gravimetry, chromatography, infrared spectrometry

Introduction

Propellants consisting of nitrocellulose and/or other nitric esters are inherently chemically unstable and undergo decomposition even under standard storage conditions. Their decomposition can be inhibited or nearly stopped when approximate stabilizers are used. However, conventional stabilizers form nitrosamines that have toxic and carcinogenic effects. Therefore, these conventional stabilizers should be replaced as soon as possible.

In general, chemical stabilizers are substances capable of the chemical binding of decomposition products of, above all, nitrocellulose and other nitroesters used for the production of smokeless powders [1]. Smokeless powders containing nitrocellulose (*NC*) or a mixture of nitrocellulose and nitroesters such as nitroglycerin (*NG*) or diethyleneglycoldinitrate (*DEGDN*) are chemically unstable due to the low binding energy (155 kJ.mol^{-1}) of the ester functional group -CH$_2$O-NO$_2$. As a result, gaseous components, especially NO$_x$, are liberated and nitric and nitrous acids are created during storage and thermal exposure. Gradual decomposition is caused both by the action of residual acids and salts that are usually sealed in nitrocellulose fibers after nitration and by the general effects of the thermal instability of nitroesters, especially during prolonged exposure or storage. Generated products react with the traces of water and their acidic nature may autocatalytically accelerate further decomposition [2]. During the last few years, the toxicity of stabilizers and their daughter products became a major issue. Today all conventional stabilizers, which are currently used in nitrocellulose-based gun and rocket propellants, are either toxic by themselves, contain toxic/carcinogenic impurities and/or produce toxic/carcinogenic daughter products during production and/or propellant aging [3]. All conventional stabilizers used for nitrocellulose-based propellants belong to (a) aromatic amines or (b) aromatic urea derivatives. The examples of (a) are alkyl-aryl-amines (e.g. p-nitro-N-methylaniline *pNMA*, p-nitro-N-ethylaniline *pNEA*) and diaryl-amines (e.g. diphenylamine *DPA*, 2-nitro-diphenylamine *2-NDPA*). The stabilizers of (b) are urea compounds in which nitrogen is substituted with diaryl (e.g. N-methyl-N´,N´-diphenylurea *Ak II*) or with alkyl-aryl (N,N´-diethyl-N,N´-diphenylurea *C I*, N,N´-dimethyl-N,N´-diphenylurea *C II*).

At present there are no alternatives for these stabilizers. Therefore, conventional stabilizers should be replaced as soon as possible. In earlier studies phenols were reviewed as possible stabilizers [4]. Furthermore, triphenylamine was examined as one of promising substances in joint tests performed by WIWEB and Explosia a.s. as well as WIWEB and Nitrochemie Wimmis AG [5-9], The papers [10] and [3] (WIWEB, G. Heeb) describe the tests of an epoxidized

oil-based stabilizer, namely lankroflex E2307 (epoxidized soybean oil), in the years 2006 to 2008. Double base and triple base powders with this substance content were formulated and subjected to the tests of chemical stability, to microcalorimetric measurement and to sensitivity tests. Very promising results made us decide to test the same stabilizer and other epoxidized oils (lankroflex L – epoxidized linseed oil and lankroflex ED6 – epoxidized mixture fatty acids, C14-22, 2-ethylhexylesters) in double base powders with different compositions and with different shapes of the final grain. The chemical structure of the new alternative stabilizers and their decomposition products should prevent the formation of toxic N-nitrosamines.

The developed powders with new stabilizers are subjected to the tests of chemical stability and to sensitivity tests. Powders containing akardite II as a conventional stabilizer are tested simultaneously and results are compared. Applied testing methods: Microcalorimetry at 89 °C, Determination of Chemical Stability at 100 °C, Weight Loss Test at 89 °C, Determination of Chemical Stability according to Bergmann-Junk, Determination of Chemical Stability by Methyl-Violet Test, Determination of Chemical Stability by Vacuum Stability Test, Determination of Explosion Heat, BAM Impact Test, BAM Friction Test and Ignition Temperature Test.

This paper concentrates on the qualitative and quantitative analyses of smokeless powders containing new stabilizers. It is necessary to determine the contents of nitroglycerin (HPLC/UV), stabilizers (akardite II – HPLC/UV, oils – gravimetry) and residual solvents (acetone, ethylacetate, ethanol – GC/FID, water – Karl Fischer titration) in the produced powder (double base powders contained *NC* and *NG* were used for this purpose.). As a rule, the sample has to be modified before these analyses. The method of sample modification will be mentioned for every method. However, Soxhlet extraction in a modified rapid extractor was the most frequent method. In the end, the paper focuses on suggesting a mechanism for stabilizing powders with new stabilizers with the aid of infrared spectrometry.

Materials and Methods

Preparation of smokeless powder samples

Double base powders contained nitrocellulose and nitroglycerin were chosen for testing. The smokeless powders in the first series are tubular powders pressed through a round copper compression nut 3 mm in diameter. The second series includes spherical powders. Table 1 shows the composition of produced

propellants, including the anticipated analyses of both series. The types of analyses differ mainly in the determination of residual solvents because different chemicals are used in the two series.

Table 1.   Composition of propellants

Abbreviation	NC [% w/w]	NG [% w/w]	Stabilizer [% w/w]	Analyses
PP0158	86.5	12.0	akardite II 1.5	* determination of acetone, ethanol, water, *NG* and stabilizers * qualitative analyses of oils
PP0159	86.5	12.0	lankroflex L 1.5	
PP0160	86.5	12.0	lankroflex E2307 1.5	
PP0161	86.5	12.0	lankroflex ED6 1.5	
YD073-9/09	84.7	13.3	akardite II 2.0	* determination of ethylacetate, water, *NG* and stabilizers * qualitative analyses of oils
YD073-10/09	84.7	13.3	lankroflex L 2.0	
YD073-11/09	84.7	13.3	lankroflex E2307 2.0	
YD073-12/09	84.7	13.3	lankroflex ED6 2.0	

Determination of residual solvents

Determination of acetone and ethanol by gas chromatography

The determination of acetone and ethanol by gas chromatography (GC) corresponds to the standard ČSN 66 8102 (part 10). GC analyses was performed with an Agilent Technologies 6850 equipped with flame ionization detector (FID) and an automatic injector with the autosampler from Agilent Technologies 7683 B Series.

Compounds were separated on a DB-WAX capillary column (30 m x 0.32 mm i.d., 0.25 μm film thickness). The column temperature was programmed from 50 °C (3 min) at 30 °C min^{-1} to 140 °C (1.5 min) and then to 190 °C at 3 °C min^{-1}. Nitrogen was used as carrier gas, the flow-rate was 6 ml min^{-1} (3 min) then programmed at 2 ml min^{-1} to 10 ml min^{-1} (20 min). Injector temperature was 250 °C, detector 320 °C, injection volume 0.2 μl. According to Table 1 the analyses involved the samples from the first series where acetone and ethanol were used for the production of propellants.

Test procedure in brief: 5 g of powder was weighed into a conical flask of an apparatus for powder decomposition; 25 ml of NaOH solution and 10 ml of an internal standard (n-hexadecane) were added. The flask was connected to a cooler that was fitted with an extension with 5 ml of n-amylalcohol. The contents of the flask were boiled slowly until complete powder decomposition (20 minutes). Then the flask was cooled down to 20 °C (10 minutes) in a water bath and part of solution in the flask was poured into a 10 ml graduated cylinder with a ground-glass joint separating layers. The top layer was poured into a vial

of the gas chromatograph and was analyzed. Measurements were evaluated by an internal standard method.

Determination of ethylacetate by gas chromatography

The determination of ethylacetate by gas chromatography was measured according to the analytical instruction PI-numbers 01-10K 05OS82/10. GC analyses were performed with a Hewlett Packard 5890 A equipped with FID and an integrator HP 3396 Series III.

Compounds were separated on a OV-17 on Chromosorb W-HP packed column (1.8 m x 2.0 mm i.d., 0.125-0.149 mm porosity). The column temperature was programmed from 75 $^{\circ}$C (2 min) at 20 $^{\circ}$C min^{-1} to 150 $^{\circ}$C (2 min). Nitrogen was used as carrier gas, the flow-rate was 12.5 ml min^{-1}. Injector temperature was 150 °C, detector 200 °C, injection 2 μl. According to Table 1 the analyses involved the samples from the second series where ethylacetate was used for the production of propellants.

Test procedure in brief: 10 g of powder was weighed into a 250 ml flask. 50 ml of toluene and 5 ml of methylacetate solution (internal standard) were added. The flask content was heated for 1 hour in water bath (80 °C). After calibration of gas chromatograph was solution in the flask analyzed. Analyses were evaluated by an internal standard method.

Determination of water by Karl Fischer titration

The determination of water by Karl Fischer titration corresponds to the standard ČSN 66 8102 (part 20, method A). Determination was performed on the equipment for electrometric titration METROHM 701 KF TITRINO and by means of the magnetic stirrer METROHM 703 Ti Stand.

A mixture of methanol and ethylacetate (2:1) was used as a powder solvent and Karl Fischer's agent Hydranal – composite 5 was used for titration. Table 1 shows that this determination involved both series of propellants.

Test procedure in brief: approximately 20 ml of a mixed solvent was measured into a titration cell. After setting the device, the solvent was titrated with Karl Fischer's agent up to the equivalence point. The process ensured the drying of the solvent before the titration of a smokeless powder sample in order not to count the water content in the solvent in the water content in the powder. Then, 0.5 g of the powder was added to the solvent while stirred on a magnetic stirrer. Solution of the sample was titrated by Fischer's agent up to the equivalence point while stirred continuously.

Determination of nitroglycerin and akardite II by liquid chromatography

The determination of nitroglycerin and akardite II by HPLC (high performance liquid chromatography) was measured according to the analytical instruction 15-PI 6802 10441. HPLC analyses was performed with an Agilent Technologies 1050, consisting of an autosampler (Agilent Technologies) and an ultraviolet detector (UV) (diode array detector - DAD, Hewlett Packard).

Compounds were separated on a SEPARON SGX C18 analytical column (250 mm x 4 mm i.d., 5 μm film thickness). The mobile phase consisted of bidistilled water – MeOH (30:70, v/v). All separations were carried out at 30 °C applying a flow-rate of 0.6 ml min^{-1}. The injection volume was 40 μl. Compounds were detected with a UV detector at 230 nm. Table 1 shows that the analyses involved both powder series.

Test procedure in brief: before analyses the powder sample had to be modified by means of a rapid extractor adjusted with Soxhlet extraction. A dry clean extraction cartridge in the extractor was charged with 2.5 g of the sample (ground on a manual mill and sieved through a screen with 1 mm meshes), covered with previously extracted cotton wool and introduced into the glass insert of the rapid extractor. 100 ml of dichlormethane (extraction agent) was measured by a 100 ml beaker into a previously dried (in a drier at 105 °C) flask in the rapid extractor. The device was assembled and extraction was carried out on a water bath for 8 hours. On the completion of the extraction dichlormethane was distilled nearly dry from the beaker on a water bath with a temperature of 70 °C. The remaining CH_2Cl_2 was blown off by a water aspirator and the extract in the flask was dried in a desiccator above concentrated H_2SO_4 until the next day. Finally, the flask with the extract was weighed and the extract content was calculated in per cents. The extract contained nitroglycerin and stabilizer (akardite II or oil, depending on the type of sample). The HPLC analyses proceeded as follows: a 250 ml glass flask with the extract was added with a required weighed amount (0.02500 to 0.02625) of an internal standard, namely dinitroxy ethyl nitramine (DINA). Then, was added 30 ml of methanol (purity p.a.) and the charge was dissolved. 0.16 ml of the solution was pipetted from the flask into a little graduated cylinder where it was added with a mobile phase (MeOH – water 1:1) to 5 ml. A small amount of material was removed from the cylinder with an injection syringe that was then fitted with a filter and the solution was filtered directly into a glass vial of an automatic sampler of the liquid chromatograph. Using the HP 1050 service program of the liquid chromatograph all extracts were analyzed and evaluated to identify the contents of *NG* and the stabilizer akardite II in respective extracts by an internal standard method.

Gravimetric determination of oils as smokeless powder stabilizers

This method is applied to determine wax, vaseline and transformer oil in smokeless powders (according to the analytical instruction 15-PI 6802 15). Unlike the basic principle of the preparation procedure, this method uses 70% (v/v) methanol, filter paper pores are 3 μm or smaller in size, and the filtrate is re-filtered. Like with HPLC/UV and IR analyses (infrared spectrometry analyses), this determination requires the preparation of smokeless powder extracts according to the principle described in previous chapter. After dissolving the extract in 70% (v/v) methanol, the solution is let stand for a maximum of 1 hour. If this time is exceeded, the oil gradually dissolves in methanol and passes through the filter together with *NG*. Table 1 shows that the analyses involved both powder series.

Test procedure: 40 ml of 70% (v/v) methanol was added into a 250 ml flask with the extract. The flask content was heated on a water bath until the complete dissolution of nitroglycerin. The components under determination were practically insoluble when cold and at this concentration (the dissolve only if let stand for a long time). Afterwards, the flask was cooled with cold water and let stand for a maximum 1 hour in a crystallization dish filled with water to allow for the separation of the component being determined. The *NG* solution was separated by filtration on filter paper and the flask was repeatedly rinsed with a small amount of methanol because a part of the determined component could get in contact with the filter. On the completion of filtration, the obtained filtrate was re-filtered on the original filter paper. Subsequently, the portion captured on the filter was quantitatively transferred into the original 250 ml flask by means of diethylether. Diethylether was evaporated on a water bath and the residual diethylether was exhausted with a water aspirator. The flask was dried in a drier at 100 °C until reaching constant weight and weighed. The oil content expressed in weight per cent was calculated based on the known charge of a sample for extraction (2.5 g), the weight of an empty flask and the identified weight of a flask filled with oil.

Qualitative analyses of smokeless powders by infrared spectrometry

This method is used for the qualitative analyses of smokeless powder samples. Close attention was paid to the absorption bands of oil stabilizers. Because they are esters of fatty acids, the occurrence of absorption bands typical of esters can be expected. The comparison of the spectra of oils as standards and of oils in smokeless powder can suggest the possible reactions of these substances in a propellant as well as the mechanism of stabilizing propelling materials by these substances. Once again, like with HPLC/UV it was necessary to perform

extraction and to measure IR spectra from extracts. The extraction is described earlier. The IR spectrum was measured only for the first powder series. The other series exhibited identical results. The measurement was carried out on an infrared spectrometer with Fourier transform IMPACT 410 with a computer station and a service program. Device parameters: 32 scans, definition: 8 cm^{-1}.

Test procedure: The measurement was carried out in a wavenumber range of 4000-600 cm^{-1}. Afterwards, the sensitivity of the device was checked. Two NaCl plates were ground together with MgO and methanol on a support, cleaned with acetone and polished. The plates were then fitted in a holder and carefully pressed against each other by means of two screws. The holder was inserted into the device and background was measured to be later deducted from the spectrum of samples. Subsequently, the holder was extended from the device and disassembled. A drop of the measured sample was dropped between the NaCl plates with a glass rod. The plates were carefully inserted into the holder, assembled and placed into the device. The spectrum of the sample was measured.

First, the oils alone were measured as standards. Afterwards, the extracts were measured. As expected, the latter measurement displayed absorption bands typical of oils that were overlapped with the bands of nitroglycerin, i.e. the second extract component. In order to measure the spectra of the oils *NG* had to be removed. The procedure consisted of measuring 20 ml of 80% (w/w) methanol and adding it to the extract in a 250 ml flask. The flask walls became covered with separated oil which is nearly insoluble at this concentration of methanol and at a cold temperature. The *NG* solution in methanol was then carefully poured away from the flask. Two more extractions with methanol were carried out. The residual material in the flask was added with a small amount of acetone of p.a. purity. The oil dissolved and acetone was placed on a water bath to evaporate nearly dry. After evaporation the acetone residue was blown off with a water aspirator. The flask was dried in a desiccator above sulfuric acid. After cooling a small amount acetone was poured into the flask and the solution was carefully poured onto one NaCl plate fastened in the holder. On the evaporation of acetone the holder was pushed into the device and the spectrum was measured.

Results and Discussion

Determination of residual solvents

Table 2 shows the contents of solvents in the first series of smokeless powder samples and Table 3 shows the contents of solvents in the second series of smokeless powder samples.

The contents of volatile substances were higher in the first series. The thorough during of samples after production failed. The samples were cut and then dried in an open air for 6 days, then in a thermostat at 55 °C for one day, and then in an open air again for 3 days. The volatile substances were analyzed. In view of their high contents the samples were dried in a laboratory drier at 55 °C for 2 days but during the night between those two days the samples were in a thermostat at 55 °C. On the second day of the drying each sample was removed from the laboratory drier and placed into a fluid drier for 90 minutes.

Table 2. Contents of solvents in the first series of smokeless powder samples

Sample	PP0158	PP0159	PP0160	PP0161
water [% w/w]	0.19	0.35	0.11	0.12
acetone [% w/w]	2.05	1.69	1.51	1.50
ethanol [% w/w]	0.99	1.51	1.50	1.44
total solvents [% w/w]	3.23	3.55	3.12	3.06

Table 3. Contents of solvents in the second series of smokeless powder samples

Sample	YD073-9/09	YD073-10/09	YD073-11/09	YD073-12/09
water [% w/w]	0.37	0.26	0.28	0.30
ethylacetate [% w/w]	0.57	0.37	0.47	0.35
total solvents [% w/w]	0.94	0.63	0.75	0.65

Determination of nitroglycerin and stabilizers

Table 4 shows the contents of *NG* and stabilizers in the first series of powder samples and Table 5 shows the contents of *NG* and stabilizers in the second series of powder samples.

Table 4. Contents of *NG* and stabilizers in the first series of powder samples

Sample	Extract [% w/w]	NG [% w/w]	Stabilizers [% w/w]	Amount remaining to the extract [% w/w]
PP0158	13.52	11.59	1.38	0.55
PP0159	13.26	11.68	0.98	0.60
PP0160	13.16	11.45	1.48	0.23
PP0161	13.15	11.38	1.06	0.71

The HPLC/UV method was applied to determine the *NG* content. In samples stabilized with akardite II this method was further used to determine the content of the stabilizer. The content of *NG* and of the stabilizer was supposed

to be 12% (w/w) and 1.5% (w/w), respectively, in the samples of the first and the second series. The *NG* and *Ak II* contents identified in the first series were approximately 11.5% (w/w) and 1.38% (w/w), respectively. The contents of *NG* and of *Ak II* identified in the second series were approximately 12.5% (w/w) and 1.70% (w/w). Figure 1 presents the chromatogram of *NG* and *Ak II* determination in the PP0158 sample.

Table 5.   Contents of *NG* and stabilizers in the second series of powder samples

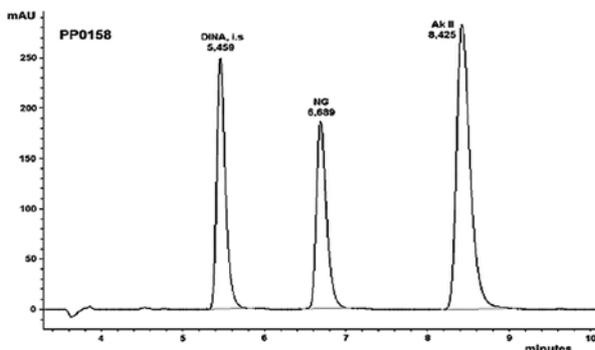| Sample	Extract [% w/w]	NG [% w/w]	Stabilizers [% w/w]	Amount remaining to the extract [% w/w]
YD073-9/09	14.82	12.59	1.70	0.53
YD073-10/09	13.02	12.40	0.51	0.11
YD073-11/09	14.09	12.46	1.36	0.27
YD073-12/09	13.64	12.25	0.70	0.69

Figure 1.   Chromatogram of *NG* and *Ak II* determination in the PP0158 sample.

Oil determination posed the greatest difficulty. The standard method of determining the contents of vaseline, wax and transformer oil failed. Oils were partially soluble and passed through a filter in 80% (v/v) methanol. The HPLC/RI (refractometric detection) analyses appeared to be a convenient option. Unfortunately, the refractometer was not sensitive enough to detect oil contents of about 1.5% (w/w). The HPLC/MS (mass detector) analyses of oils are preferred in the case of qualitative analyses. Oil contents determination at a semiquantitative scale was not successful either. One of the available options was the derivatization of oils methylesters and the subsequent GC/FID or GC/MS analyses. MSTFA-based derivatization is considered (N-methyl-N,N-trimethylsilyl trifluoroacetamid). Analyses proceeded on a DB-5HT column

that can resist temperatures up to 460 °C. This method could be used to verify the proposed mechanism of powder stabilization with oils (see next chapter).
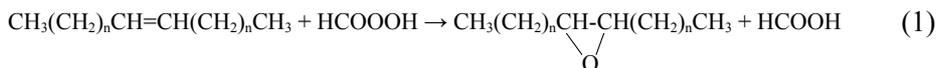
To begin with, the modification of vaseline, wax, and transformer oil determination with the above-referenced apothecary balance was selected. This modification consists of using 70% (v/v) methanol in which the oils applied are virtually insoluble while *NG* is still soluble (it is insoluble in less concentrated methanol) and of using an extremely thick filter with pores that are 3 μm and smaller. The filtrate has to be filtered repeatedly and the maximum standing time of the extract with methanol (1 hour) must be observed. The content of lankroflex L in the first and second series was 0.98% (w/w) and 0.51% (w/w), respectively (as opposed to the anticipated 1.5% in either case). The first series contained 1.48% (w/w) of lankroflex E2307 (as opposed to the anticipated 1.5%) and the second series contained 1.36% (w/w) (as opposed to the anticipated 1.5%). The first series contained 1.06% (w/w) of lankroflex ED6 (as opposed to the anticipated 1.5%) and the second series contained 0.7% (w/w) (as opposed to the anticipated 1.5%). Interestingly enough the anticipated content of lankroflex E2307 was detected in every sample. The contents of the two other oils were lower, sometimes markedly so. This finding implied that lankroflex E2307 (soybean oil) exhibits perhaps better compatibility with *NC* and *NG* that the two other oils. Those oils are most likely liberated from a propellant in the course of its production, for instance during the drying kneading of the powder mass.

Tables 4 and 5 also present the calculation of the amount remaining to the extract amount. If we add up the contents of *NG* and of the stabilizer, we get the total contents of the extract in weight per cent. This value can be compared with the value calculated directly from extraction. Deviations of up to 0.5% (w/w) are common extraction errors.

Qualitative analyses of smokeless powders by infrared spectrometry

Infrared spectrometry was applied in order to identify the form in which oil stabilizers are found in powder samples. After measuring the oils alone and according to previous assumptions, it was identified that the oils were the esters of fatty acids (the infrared spectrum is in Figure 2, Table 6). It has to be specified that they are epoxidized oils. After removing *NG* (the infrared spectrum is in Figure 3, Table 6) from the extract the spectra of the oils proper contained in powder samples were measured (the infrared spectrum is in Figure 4, Table 6). The bands of esters were visible again. As expected, a wide band of OH-group valence vibrations was also observed. This implies the possible mechanism of the stabilization of powders by these oils. The stabilizer is known to capture the oxides of nitrogen liberated during *NG* and *NC* decomposition. NO_x may then

accelerate the further decomposition of an explosive. It is already known from organic analyses that epoxides, i.e. three-member cyclic ethers, are unstable in an acidic environment and decompose to alcohols, namely diols. However, the acidic environment does not exist in smokeless powder. In addition to acidic NO_x, *NC* contains the remainders of nitric acid from the nitration of cellulose. The epoxidation of oils is expressed by the following equation:

$$CH_3(CH_2)_nCH=CH(CH_2)_nCH_3 + HCOOOH \rightarrow CH_3(CH_2)_n\underset{\diagdown O \diagup}{CH\text{-}CH}(CH_2)_nCH_3 + HCOOH \qquad (1)$$

Because powder contains an acidic environment epoxide decomposition follows this reaction:

$$CH_3(CH_2)_n\underset{\diagdown O}{CH\text{-}CH}(CH_2)_nCH_3 + H^+ \rightarrow CH_3(CH_2)_nCH(OH)\text{-}CH(OH)(CH_2)_nCH_3 \qquad (2)$$
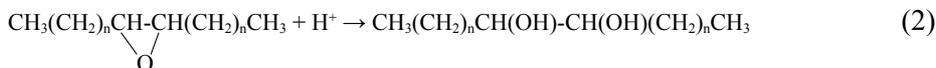
The subsequent possible mechanisms of stabilizing smokeless powders are:
- reduction of NO_x (especially NO_2) to nitrogen N_2, while alcohols acting as reducing agents are oxidized to carbonyl compounds:

$$CH_3(CH_2)_nCH(OH)\text{-}CH(OH)(CH_2)_nCH_3 + NO_x \rightarrow N_2 + 2\ CH_3(CH_2)_nCH=O \qquad (3)$$
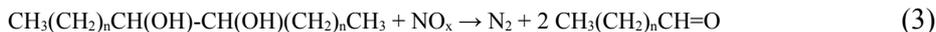
- or the creation of the bond RCH-O-NO or RCH-O-NO_2, a hydroxy compound nitrate.

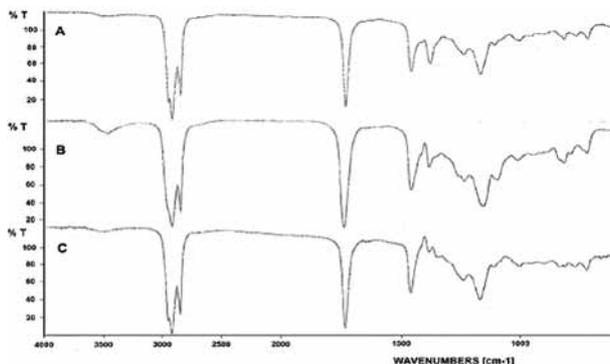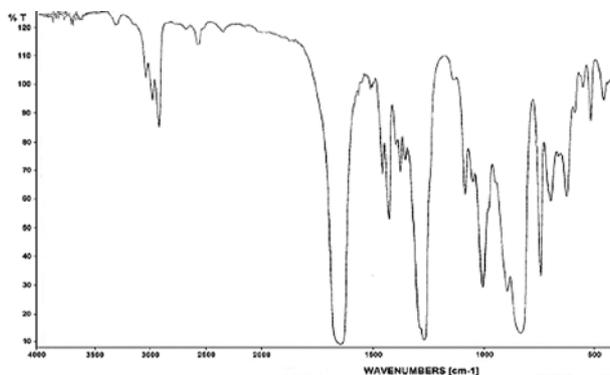The mechanism of stabilizing powders with oil stabilizers may be pursued in further studies.

Figure 2.   The IR spectrum of pure oils; A – lankroflex ED6, B – lankroflex L, C – lankroflex E2307.

Table 6.   Evaluation of infrared spectra

Substance	Wavenumber [cm^{-1}]	Functional group
oils: lankroflex L lankroflex E2307 lankroflex ED6	~ 2950-2850 υ_{ASYM} + υ_{SYM}	-CH$_3$, -CH$_2$, ?-CH
	~ 1730 δ	-C=O of esters
	~ 1460-1380 δ_{ASYM}+δ_{SYM}	-CH$_3$, -CH$_2$, ?-CH
	~ 1170 δ	-C-O-C of esters
	~ 1100-700	skeletal vibration
	~ 720 ρ (rocking)	(CH$_2$)$_n$, n>4
NG	~ 2950-2850 υ_{ASYM} + υ_{SYM}	-CH$_2$, -CH
	~ 1650 υ_{ASYM}	-NO$_2$
	~ 1470-1380 δ_{ASYM}+δ_{SYM}	-CH$_2$, -CH
	~ 1300 υ_{SYM}	-NO$_2$
	~ 1100-500	skeletal vibration
extracts after removal of NG. PP0159 PP0160 PP0161	~ 3400 υ	-OH
	~ 2950-2850 υ_{ASYM} + υ_{SYM}	-CH$_3$, -CH$_2$, ?-CH
	~ 1730 υ	-C=O of esters
	~ 1650 υ_{ASYM}	-NO$_2$, rest of NG
	~ 1460-1380 δ_{ASYM}+δ_{SYM}	hangers -CH$_3$, -CH$_2$, ?-CH
	~ 1350 υ_{SYM}	-NO$_2$, rest of NG
	~ 1100 υ+δ	-C-O + -OH

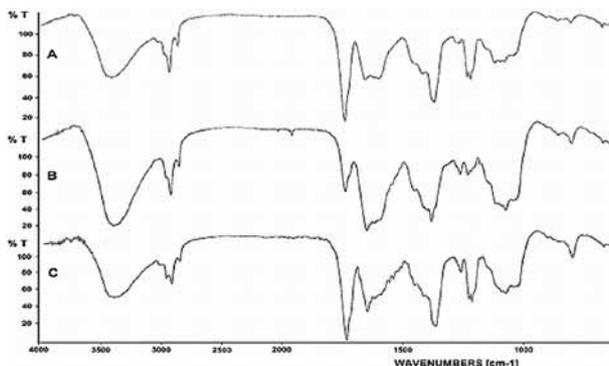**Figure 3.**   The IR spectrum of NG.

Figure 4. The IR spectrum of after the removal of *NG*; A - PP0159, B - PP0160, C - PP0161 samples.

Conclusion

This paper is part of a study dealing with the use of new nontoxic stabilizers in smokeless powders. The stabilizers applied in the study are epoxidized vegetable oils that, unlike conventional stabilizers meet the current requirements for toxicity affecting man and the environment. In addition to a number of stability tests that show to what degree oils stabilize powders in comparison with conventional stabilizers, it is necessary to carry out both the quantitative and qualitative analyses of smokeless powders. The main aim of this paper was to suggest a method that would successfully determine oils in a powder. The applied apothecary balance method meets the requirements for the determination of oils. However, the obtained results should be compared with another method based on a different principle (the use of gas chromatography is considered) in order to identify possible losses and errors. As a result, the conditions of the apothecary balance method would be modified or the method would be completely replaced. Another objective of this paper was to suggest a mechanism of stabilizing powders with oils. The application of infrared spectroscopy appears to be approximate for this purpose provided that nitroglycerin is first separated from oils because nitroglycerin bands in the infrared spectrum significantly overlap the bands that are typical of oils. Detailed discussion is in the previous chapter. Like in the determination of oils, the proposed mechanism has to be verified by another method, ideally by gas chromatography with weight detection.

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