Central European Journal of Energetic Materials, **2014**, *11*(4), 613-624
ISSN 2353-1843

An Investigation of the Extended Storage of Single-base Propellants

Milena NEDKOVA, Petar SHISHKOV, Lina VARADINOVA, Ivan GLAVCHEV*

University of Chemical Technology and Metallurgy, 8 Kl. Ohridski bvds, Sofia, Bulgaria
**E-mail: ivgl@uctm.edu*

Abstract: An investigation of single-base propellants has been conducted. The ageing process during extended storage of single-base propellants (SBP) in non-heated military stores and a heated building has been investigated by elemental analysis. Two or three different absorbencies around the band at 1650 cm^{-1} were observed by FTIR spectroscopy. In this way, not only the denitration of the propellants was determined, but also cleavage of -O-C- bonds between the glycoside rings in the nitrocellulose macromolecules. The latter process was confirmed by the swelling of the SBP.

Keywords: ageing, single-base propellants, elemental analysis, FTIR, swelling

1 Introduction

The issue of ageing of single-base propellants (SBPs) has been investigated by many organizations because of its importance. Usually the process investigated is that of changes in the stabilizers [1-3]. It is known that the nitrogen content of the SBP is very important. This characteristic is determined by several methods, among which Lunge's method is the standard [4]. For example, in [5] elemental analysis was applied for the determination of the nitrogen content, and in [6] alkaline hydrolysis and ion chromatography were applied in the determination of the nitrogen content of samples of gunpowder, produced in 1944 and 1993, and of samples of collodion. In the present work we have devised a new method for the measurement of the nitrogen content of SBPs which had been produced several

years ago. In our article [7] we described the observation of 3 maxima around 1650 cm^{-1} in the IR spectra of SBPs stored over a long period. The explanation of these bands was the formation of low-molecular weight fractions of the SBPs during their ageing. In [8, 9] the observation of several maxima around the band at 1650 cm^{-1} for nitrogen containing compounds was reported. According to [10] low molecular weight nitrogen containing compounds exhibit 2 or 3 maxima for $–ONO_2$ in their IR spectra around the band at 1650 cm^{-1}. These maxima were interpreted as being the result of possible conformations of the molecules of these compounds. The IR spectra, published in [7] were made with a Perkin Elmer (USA) apparatus and were not made for quantitative IR analysis in the 30-70% absorbance region. The IR spectra were recorded several years ago. Therefore, the current investigation had to verify these observations.

The swelling of an SBP in solvents depends mainly on its properties. The SBP nitrogen content, molecular weight and other characteristics are reasons for its varying interaction with different solvents. Thus, the current results can be applied to an explanation of the ageing of SBPs. The results obtained are summarized in this communication.

2 Experimental

Samples from 7 SBP channels, products from "Arsenal" Ltd. Bulgaria, had been stored in non-heated military stores, in silk pouches in the cartridge – cases of gun shells, placed in wooden boxes from their production until the weapons were dismantled in 1990. Afterwards, until 2013, the SBP samples were stored at room temperature and in a dry atmosphere in a metal cupboard in the laboratory of the University of Chemical Technology and Metallurgy (UCTM), Sofia. Thus, the samples of SBP had been aged in the absence of light. The nitrogen content has been measured by both Lunge's method and a new method using apparatus Euro EA 3000 (Euro Vector Sp A, Italy). The carbon, nitrogen and hydrogen content were measured by burning the samples, weight 0.5-1.5 mg, at 980 ºC in an oxygen atmosphere. The gas mixture produced was passed through a chemical/absorption zone. Subsequently CO_2, N_2 and H_2O were separated by gas chromatography. A standard curve was constructed through analysis of acetanilide (C_8H_9NO, N-phenylacetamide) using the computer product Calligus. In this way it was possible to analyze different parts of the SBP samples, the analyzed material weight being around 0.1 g. The SBP samples were granules of weight around 1.8 g. FTIR spectra were obtained with thin layers using an FTIR apparatus (Varian, Germany). In order to obtain thin layers with uniform

thickness, solutions of the SBPs were made up in 25 mL measuring flasks with measured amounts of propellant (accuracy 0.0001 g) dissolved in acetone, p.a., a product of Valerus Ltd., Bulgaria. Then the solvent was evaporated and the SBPs remained as a coating. The IR spectra were recorded and the values of some peaks with "base line" were calculated according to Equation (1):

$$A = \log (100 - i) / I \quad (1)$$

where: i is the distance from the crossing point of the "base line" with the line, passed from the peaks to the absorption of 100%, I is the distance from the top of the peak to absorption 0%.

Spectra using 70 scans were recorded. Using an internal standard (i.s.) absorption at 1160 cm^{-1}, the values of A^* were calculated using Equation (2):

$$A^* = A / A_{(i.s.)} \quad (2)$$

The swelling of the SBP samples was measured on samples weighed with an accuracy of 0.0001 g, in test tubes with diameter 7 mm, and a calculated quantity of acetone, p.a., a product of Valerus Ltd., Bulgaria. The SBP : acetone ratio = 1 : 1. Two test tubes for each sample were measured and the average values of the swelling after different swelling times at temperatures t_1 = 19 ºC and t_2 = 40 ºC were calculated. The area of the samples was measured with an accuracy of 0.001 mm. The time of swelling was measured with an accuracy of 0.01 s using a stop watch.

3 Results and Discussion

The nitrogen content measurements were made according to Lunge's method and are given in [11], and the values of $\Delta = (N_{[11]} - N_{av})\%$ was calculated, where $N_{[11]}$ was the nitrogen content made with Lunge's method and published in [11], N_{av} was the nitrogen content measured with the new method. The results, obtained with the new method, were measured twice in order to define the error, and the values of Δ_A were calculated. The results, obtained for the current study and for the same SBP samples are given in Table 1.

- The differences between the results for the nitrogen content, made with the new apparatus and with the standard Lunge's method were small (Δ values).
- The differences between the results for the nitrogen content, made with the new apparatus were small (Δ_A values).

- The new method used small sample weights.
- The ageing runs from the external (outside) surface of the SBP granules to their inside.

Table 1. Results from elemental analyses of SBP samples and for Δ and Δ_A

Year of production	N [%]	C [%]	H [%]	Sample weight, [mg]	Correlation	Δ_A [%]	Δ [%]
1944	12.969 13.089	12.969	2.986	1.240	N - 0 99989	1.45	0.92
1955	12.423 12.838	25.950	2.962	-	N - 0.99979	3.74	3.23
1959	12.642 12.935	25.694	2.822	0.940	N - 0 99989	2.66	2.27
1962* inside	11.899 11.739	27.202	3.015	1.040	N - 0 99989	-	1.3
1962* outside	12.629 12.277	28.213	2.940	1.370	N - 0 99989	-	2.87
1983	12,789 12.998	29.437	3.015	0.720	N - 0 99989	1.93	2.61

* inside, outside – location of samples removed for elemental analyses from the propellant granules

Reference [7] gives the IR spectra of the SBP samples produced by "Arsenal" Ltd. Bulgaria. In that investigation the FTIR spectra were recorded for the same propellants, but in the absorbance region 70-30%, available for quantitative IR analysis. On the other hand our FTIR spectra were recorded using 70 scans and were calculated using not only the absorbance of the bands, but of the shoulders too. For increased accuracy the FTIR spectra were recorded using thin layers of the solutions of SBP in acetone, p.a.; the results are given in Table 2. It was evident, that the solutions used had concentrations, smaller than 5% and had small differences in their values.

Table 2. Data for solutions of SBPs in acetone, p.a.

Year of production	Period of ageing [years]	G sample [g]	Concentration [g/mL]
1944	(46) + 23	0.7403	2.96
1955	(35) + 23	0.6663	2.67
1959	(31) + 23	0.6648	2.66
1962	(28) + 23	-	-
1983	(7) + 23	1.0737	4.3

The period (years) of ageing of the SBPs in non-heated military stores is given in parenthesis, the period (years) of ageing of the SBPs in heated building is given without parenthesis.

For greater accuracy the FTIR spectra were recorded several times and the values of the absorbencies for the $-ONO_2$ groups were calculated. The results obtained are presented in Table 3. The values of Δ_1,% were calculated by Equation (3) only for data in [7] for the band at 836.2013 cm^{-1}, because this was from absorbance 92-55%.

$$\Delta_{836},\% = A^*_{836,2013} - A^*_{836,1993} / A^*_{836,2013} \quad (3)$$

Table 3. A^* values of some maxima from the FTIR spectra of samples of SBP

Year of production	Period of ageing [years]	$A^*_{1653\ cm^{-1}}$	$A^*_{1278\ cm^{-1}}$	$A^*_{836\ cm^{-1}}$	Δ_{836} [%]
1944	(46) + 23	4.062	4.6321	2.6707	26.707
1955	(35) + 23	4.5344	5.0134	3.2996	53.731
1959	(31) + 23	5.4328	6.0992	3.7024	-
1983	(7) + 23	5.0616	5.5018	3.6463	50.419

It is evident that for the values of Δ_{836}, the percentages were very large, because the spectra, published in [7], were not recorded in the region available for quantitative IR analysis. From the data given in Table 3, it was evident that the values of A^* paced through maximum for samples of SBP, made in 1959. The values for A^* at 1278 cm^{-1} in all samples were maximal. The values of the area (S) of some bands in the FTIR spectra are given in Table 4.

Table 4. Data for the area (S) of some bands in the FTIR spectra of SBP samples

Year of production	Period of ageing, [years]	S_{1652} [mm^2]	S_{1652}/S_{1160}	S_{837} [mm^2]	S_{837}/S_{1160}
1944	(46) + 23	1702.19	7.7353	1796.65	8.1696
1955	(35) + 23	1501.6	9.1221	1476.863	8.9718
1959	(31) + 23	1683.527	13.9657	1150.292	9.657
1962	(28) + 23	-	-	-	-
1983	(7) + 23	1401.004	8.8625	1371.348	8.6749

It is evident, that there is one and the same dependency between the values of S for the SBP samples and the A^* for different bands in the FTIR spectra. In this study, conclusions were made only using A^*, because it was possible to

measure these values for the bands (peaks) and the shoulders. The values of A^* for the peaks and shoulders around the band at 1650 cm^{-1} are shown in Table 5.

Table 5. The values of A^* of the peaks and shoulders around the band with absorbance 1650 cm^{-1}

Year of production	Period of ageing, [years]	$A^*_{1647\ cm^{-1}}$	$A^*_{1653\ cm^{-1}}$	$A^*_{1667\ cm^{-1}}$	$A^*_{1682\ cm^{-1}}$
1944	(46) + 23	4.3896	5.2312	3.6613*	2.1669*
1955	(35) + 23	4.3831	4.4597	4.1273*	3.6478*
1959	(31) + 23	5.1744	5.115	4.6286	4.0886*
1983	(7) + 23	4.3696	4.4334	3.9784	3.5508

The values of A^* for the shoulders in the FTIR spectra are marked with an asterisk (*). It was evident that samples of SBP have 4 bands or bands and shoulders. The FTIR spectra of samples of SBP, manufactured in 1944, 1955, 1959 and 1983, are shown in Figures 1, 2, 3 and 4 respectively.

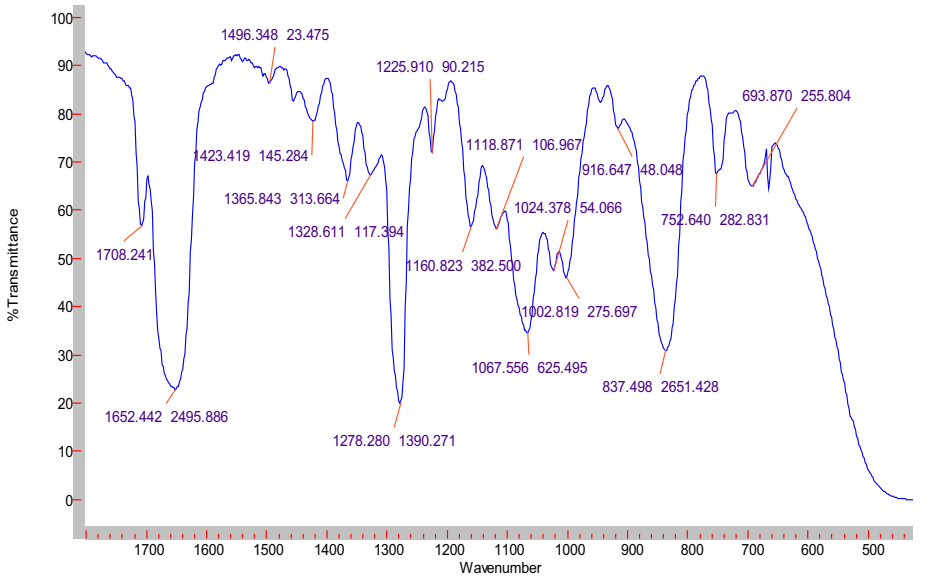
It is known that the interaction of high molecular weight compounds with solvents is dependent upon their molecular weight and begins with swelling – increasing the volume of the polymers with the mass of the solvents. This process is characterized by the rate and the degree of swelling. The rate of swelling $W = dx/dt$ was determined by Equation (4):

$$dx/dt = k\cdot(\alpha_{max} - \alpha_\tau) \tag{4}$$

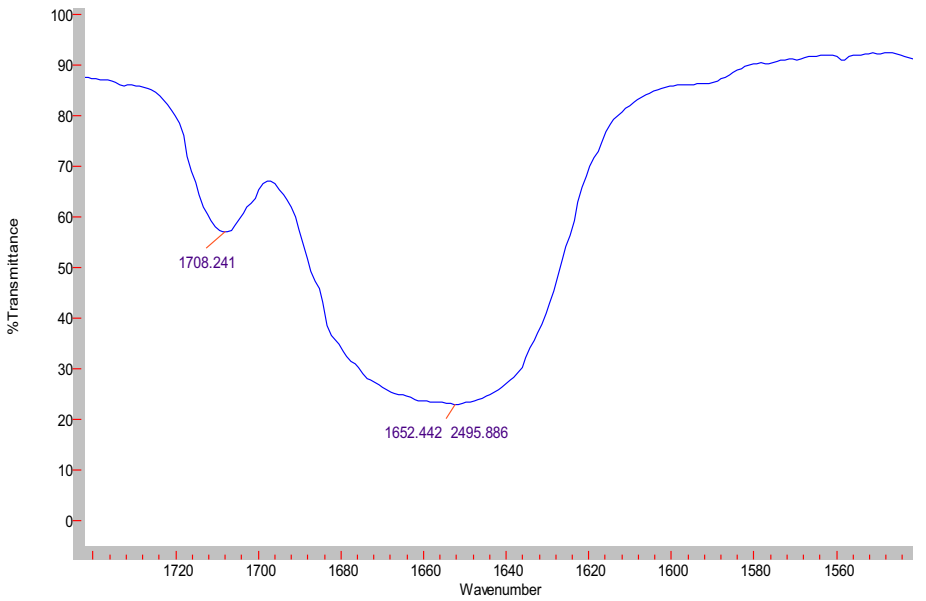
where k is the rate constant, and α_{max} and α_τ are different degrees of swelling.

From this equation it is possible to calculate the values of k using Equation (5):

$$k = 1/t \cdot \ln \alpha_{max}/\alpha_{max} - \alpha_\tau \tag{5}$$

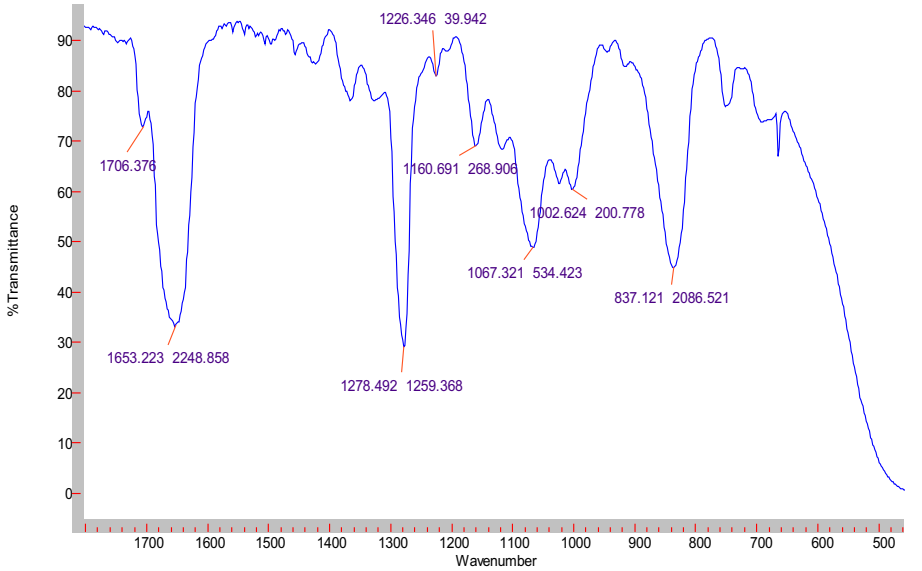


a

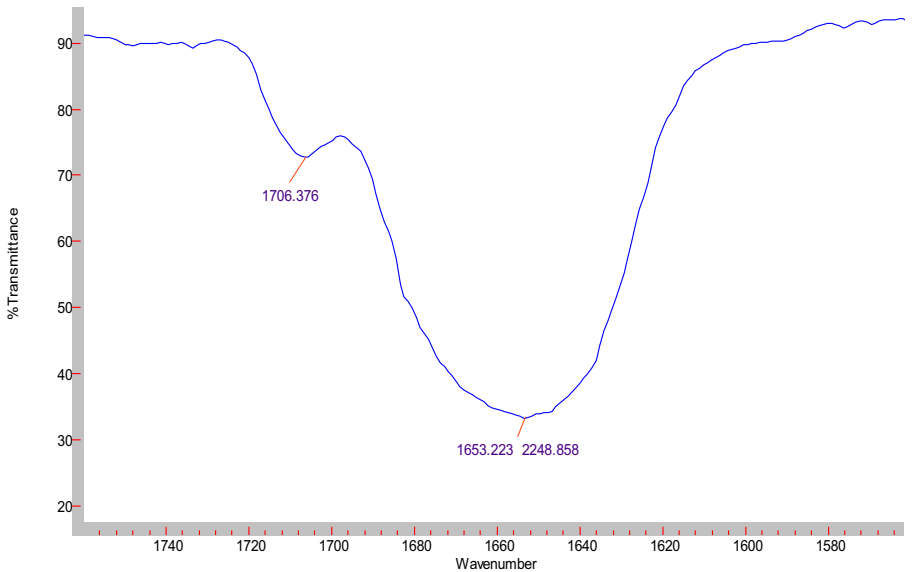


b

Figure 1. (**a** and **b**). FTIR spectra of SBP produced in 1944.

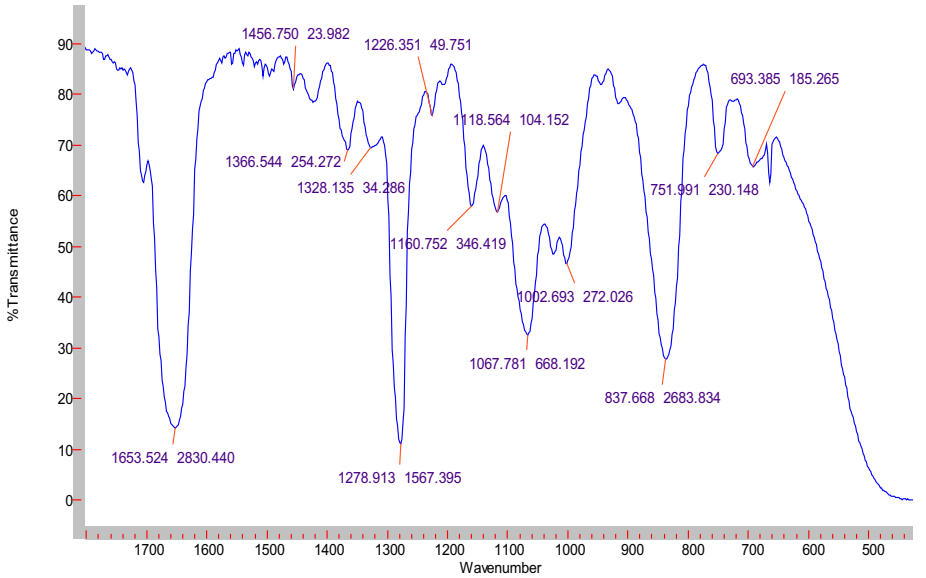


a

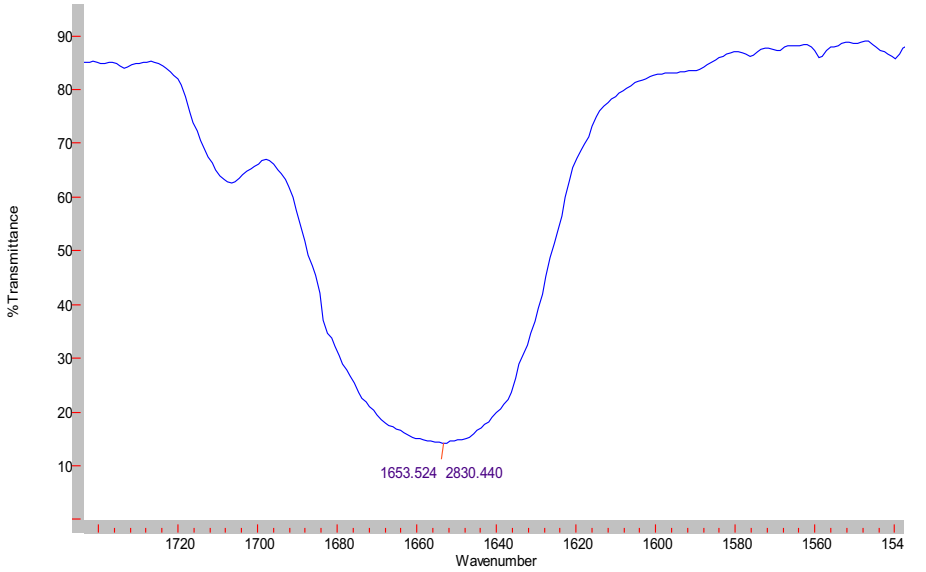


b

Figure 2. (**a** and **b**). FTIR spectra of SBP produced in 1955.

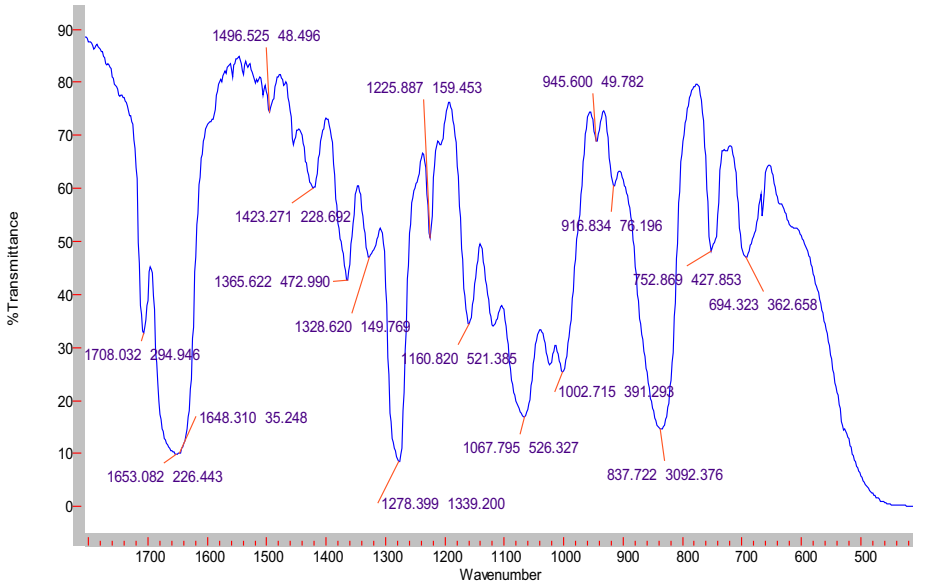


a

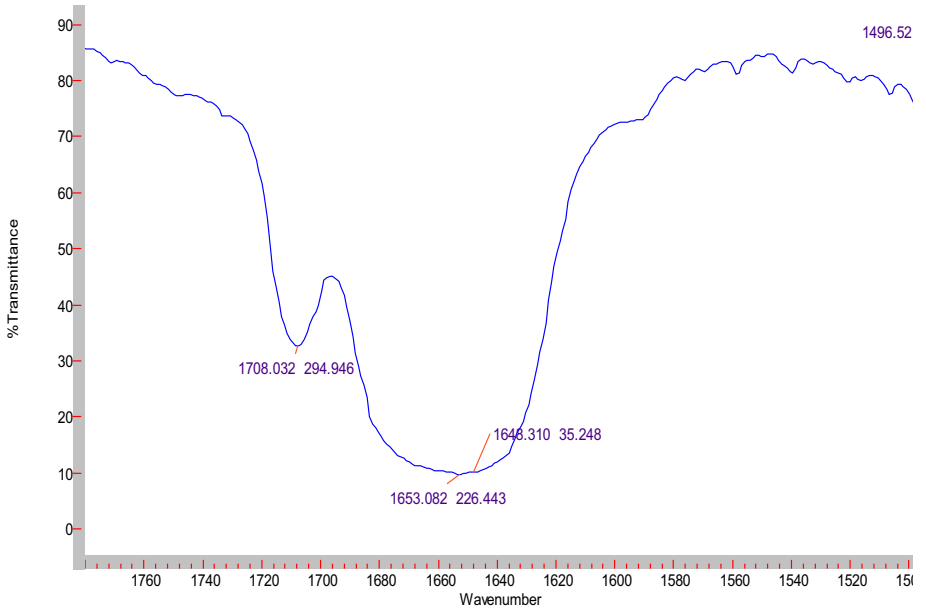


b

Figure 3. (**a** and **b**). FTIR spectra of SBP produced in 1959.



a



b

Figure 4. (**a** and **b**). FTIR spectra of SBP produced in 1983.

The rate of the process is equal to tgα of the stretch line, drawn through the maximal slop of dependence *vs.* time, in this case $\alpha_{max} = 92$. The results obtained are shown in Table 6.

Table 6. Values from the swelling of SBPs

Year of production	Period of ageing [years]	W [%/s/cm^2]	α_t [%]	$k \times 10^4$
1944	(46) + 23	t_1: 17.17 t_2: 18.55	34.1 5.26	0.2966 0.2139
1955	(35) + 23	t_1: 16.34 t_2: 16.55	19.59 21.01	0.2257 0.2331
1959	(31) + 23	t_1: 15.00 t_2: 18.20	18.18 15.39	0.2032 0.2376
1983	(7) + 23	t_1: 5.201 t_2: 8.75	6.78 4.49	0.061 0.0999
1983	(7) + 12	t_1: 4.83 t_2: 6.33	2.69 2.79	0.054 0.071

It is evident, that with ageing of the SBPs, the values of W, α_t and k increase.

4 Conclusions

The values for swelling confirmed the results, obtained with elemental analyses and FTIR spectroscopy – SBP ageing occurs not only by denitration, but also by cleavage of the oxygen bridges between the glycoside rings and thus by the creation of low molecular weight fractions of SBP.

5 References

[1] Jelisavac L., Filipovic M., Determination of Diphenylamine and Its Mono-derivatives in Single-base Gun Propellants During Aging by High Performance Liquid Chromatography, *Chromatographia*, **2002**, *55*(3-4), 239-241.

[2] Druet L., Asselin M., A Review of Stability Test Methods for Gun and Mortar Propellants, I: The Chemistry of Propellant Ageing, *J. Energ. Mater.*, **1988**, *6*(1-2), 27-43.

[3] Venter A., Ifa D.R, Cooks R.G., Poehlein S.H., Chain A., Eliason D., A Desorption Electrospray Ionization Mass Spectrometry Study of Aging Products of Diphenylamine Stabilizer in Double-base Propellants, *Propellants Explos.*

Pyrotech., **2006**, *31*(6), 472-476.
[4] *Bulgarian State Standard for Determination of Nitrogen Content by Method of Lunge*, BSS N 1525-78, **1978**.
[5] Verschragen P., Comparative Investigation of some Methods for the Determination of the Nitrogen Content of Nitrocellulose, *Anal. Chim. Acta*, **1955**, *12*, 227-230.
[6] López-López M., Alegre J.M., García-Ruiz C., Torre M., Determination of the Nitrogen Content of Nitrocellulose from Smokeless Gunpowders and Collodions by Alkaline Hydrolysis and Ion Chromatography, *Anal. Chim. Acta*, 2011, *685*(2), 196-203.
[7] Ganev R., Glavchev I., Tzvetkov T., Ivanova M., Totev T., Investigation of Long Term Ageing of Single-based Propellants, *J. Explos. Propellants, R.O.C. (Huoyao Jishu)*, **2004**, *20*(1), 7.
[8] Sanders C.W., Taylor L.T., Solution Infrared and Nuclear Magnetic Resonance of Cellulose Nitrates, *Appl. Spectrosc.*, **1991**, *45*, 604.
[9] Sanders C.W., Taylor L.T., Determination of the Degree of Nitration of Cellulose Natures via GP/FT IR, Using an Online Flow Cell, *Appl. Spectrosc.*, **1991**, *45*, 900.
[10] Prihodenko L.K., Kolosova T.E., IR Cryoscopy Investigation of Low Molecular Cellulose Nitrates (in Russian), *J. Appl. Spectrosc.*, **1992**, *56*, 294.
[11] Ganev R., Glavchev Iv., IR Spectroscopy Characterization of Single-base Propellants during Their Natural Aging, *J. Techn. Phys*., **2004**, *45*(4), 301-308.