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Comparative characteristics of sterically hindered phenols and nitroxide radicals as stabilizers of polyethylene photodegradation [*]

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Сравнительная характеристика пространственно-затрудненных фенолов и нитроксильных радикалов как стабилизаторов фотодеструкции полиэтилена[***]

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Introduction. Polymeric materials (PM) are increasingly used in various industries and agriculture. Under the action of UV light, PM are destroyed. UV stabilizers are used to protect PM from photodegradation. Their action is based on the absorption of the photoactive sunlight component or on the deactivation of excited molecules that have already absorbed a light quantum, as well as on the inhibition of dark light-induced reactions. The work objective is to provide a comparative analysis of compounds of the sterically hindered phenols (SHP) series and nitroxide radicals (NR) as the PM photodegradation inhibitors.

Materials and Methods. Reagents of the "purum" grade, LDPE premium grade 15803-020 polyethylene film were used for the investigations. The stabilizer was applied to the film by dipping. Carbonyl groups in polyethylene were determined by IR spectroscopy. IR spectra were recorded on Varian-640 instrument.

*Research Results****.*** 2,4,6-tri-tert-amylphenol (1), 2-methyl-4,6-di-tert-butylphenol (2), 4-acetylamino-2,2,6,6-tetramethylpiperidin-1-oxyl (3), 3-carboxamido-2,2,5,5-tetramethylpyrrolin-1-oxyl (4) were tested as stabilizers for photo-oxidative degradation of polyethylene. It is known that the accumulation of carbonyl and hydroxyl groups is recorded in PM samples under irradiation in the process of photodegradation through the IR spectroscopy. The absorption band of the carbonyl group at 1720 cm^{-1} appears in the IR spectra of oxidized polyethylene. The IR spectra analysis shows that the content of carbonyl groups in the check samples is significantly higher than in the samples treated by stabilizer solutions.

Введение. Полимерные материалы (ПМ) все шире используются в различных отраслях промышленности и сельского хозяйства. Под действием УФ-света ПМ разрушаются. Для защиты ПМ от фотодеструкции применяются УФ-стабилизаторы. Их действие основано на поглощении фотохимически активной компоненты солнечного света или на деактивации возбужденных молекул, уже поглотивших квант света, а также на торможении темновых реакций, индуцированных светом. Цель работы — сравнительный анализ соединений из ряда пространственно-затрудненных фенолов (ПЗФ) и нитроксильных радикалов (НР) в качестве ингибиторов фотодеструкции ПМ.

Материалы и методы. Для исследования использовали реактивы квалификации «ч», полиэтиленовую пленку ПЭВД в/с 15803-020. Стабилизатор наносили на пленки методом окунания. Карбонильные группы в полиэтилене определяли методом ИК-спектроскопии. ИК-спектры регистрировали на приборе Varian-640.

Результаты исследования. В качестве стабилизаторов фотоокислительной деструкции полиэтилена испытаны 2,4,6-три-трет-амилфенола (1), 2-метил-4,6-ди-трет-бутилфенола (2), 4-ацетиламино-2,2,6,6-тетраметилпиперидин-1-оксила (3), 3-карбоксамидо-2,2,5,5-тетраметилпирролин-1-оксила (4).

Известно, что при облучении в образцах ПМ в процессе фотодеструкции методом ИК-спектроскопии фиксируется накопление карбонильных и гидроксильных групп. В ИК-спектрах окисленного полиэтилена появляется полоса поглощения карбонильной группой при 1720 см$^{-1}$. Анализ ИК-спектров показывает, что содержание карбонильных групп в контрольных образцах значительно выше, чем в образцах, обработанных растворами стабилизаторов.

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[*] The research is done within the frame of the independent R&D.

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Discussion and Conclusions. The experiments show that nitroxide radicals of 3-carboxamido-2,2,5,5-tetramethylpyrrolin-1-oxyl series and 4-acetylamino-2,2,6,6-tetramethylpiperidin-1-oxyl are the best photostabilizers of polyethylene. Moreover, there is no significant difference between the radicals of the 2,2,6,6-tetramethylpiperidine and 2,2,5,5-tetramethylpyrroline series. Sterically hindered phenols, under photodegradation, have a far smaller stabilizing effect, falling short of nitroxide radicals.

Keywords: polyethylene, photostabilizers, phenols, nitroxide radicals.

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Обсуждение и заключения. Эксперименты показали, что лучшими фотостабилизаторами полиэтилена являются нитроксильные радикалы 3-карбоксамидо-2,2,5,5-тетраметилпирролин-1-оксил и 4-ацетиламино-2,2,6,6-тетраметилпиперидин-1-оксил. Причем нет существенной разницы между радикалами ряда 2,2,6,6-тетраметилпиперидина и 2,2,5,5-тетраметилпирролина. Пространственно-затрудненные фенолы в условиях фотодеструкции оказывают значительно меньшее стабилизирующее действие, уступая нитроксильным радикалам.

Ключевые слова: полиэтилен, фотостабилизаторы, фенолы, нитроксильные радикалы.

Образец для цитирования: Сравнительная характеристика пространственно-затрудненных фенолов и нитроксильных радикалов как стабилизаторов фотодеструкции полиэтилена / И. Ю. Жукова [и др.] // Вестник Дон. гос. техн. ун-та. — 2019. — Т. 19, № 2. — С. 151−157. https://doi.org/10.23947/1992-5980-2019-19-2-151-157

Introduction. Polymeric materials (PM) are increasingly used in various industries and agriculture. With a sufficiently high resistance to climatic factors, the PM performance decreases when affected by humidity and temperature, as well as the ultraviolet (UV) component of the solar spectrum: in this case, radical particles are generated in the polymer, and transformations that cause material destruction occur [1, 2]. If in a PM there are products of its oxidation, for example, ketones, then they are photoinitiators of the decomposition process of the polymer. To protect the PM, it is required to ensure the interaction of radicals and highly efficient light stabilizers [3]. For this purpose, UV stabilizers are used which can act as follows:

- they absorb photoactive components of the sunlight;
- they deactivate excited molecules that have already absorbed a quantum of light;
- they inhibit dark light-induced reactions;
- they destroy or deactivate photoactive impurities and photoreaction products [4, 5].

Sterically hindered phenols (SHP), sterically hindered amines (SHA), and nitroxide radicals (NR) are widely used as UV stabilizers for polymers [6, 7]. The SHP act as chain terminators. Since the addition of mobile hydrogen to the primary radicals of the polymer photolysis is an oxidative reaction, the stabilizers themselves are easily oxidized [3]. Under photodegradation, the SHA form stable NR interacting with the alkyls of polymers which causes the photodegradation chain breaking [2].

The work objective is to provide a comparative analysis of compounds from the SHP and NR series as the PM photodegradation inhibitors.

Materials and Methods. Reagents of the “purum” grade of the Aldrich company, and high-pressure polyethylene film (LDPE 15803-020, GOST 16.337-77) 0.2 mm thick were used for the investigations. Photo-oxidative degradation stabilizers of the compound:

- from the NR series – 3-carboxamido-2,2,5,5-tetramethylpyrrolin-1-oxyl (1), 4-acetylamino-2,2,6,6-tetramethylpiperidine-1-oxyl (2);
- from the SHP series – 2-methyl-4,6-di-tert-butylphenol (3) and 2,4,6-tri-tert-amyl-phenol (4).

The surface treatment of the film for applying stabilizer solutions was carried out as follows: samples of 5×5 cm were fixed in a cassette without damaging the working part of the sample, washed in warm water, blotted with cotton cloth, degreased in acetone and dried for three minutes in air at 20 –25^{0}C.

To prepare stabilizer solutions, 50 ml of toluene were poured in each of twelve 100 ml capacity measuring flasks, and the stabilizers (1–4) were added in a volume of 0.01; 0.005; 0.0025 mol. Then, the contents of the flasks were made up to the mark with a solvent. The resulting solutions were used to process film samples.

The prepared film was dipped into a beaker with the solution of a UV stabilizer [8, 9] of the desired concentration for 30–40 min. Then, the sample was removed from the solution and kept over the beaker for 3–5 minutes so that the excess solution drained from the treated surface. The sample was completely dried being suspended.

For each stabilizer solution concentration, 5 film samples were tested. 120 samples were tested in total: 60 pieces – under the natural conditions and as many – under the simulated conditions. 10 check samples (CS) were not treated with stabilizers.

After testing, the IR spectra of the check and experimental samples were taken. IR spectroscopy determined the content of carbonyl groups in the samples [10, 11]. IR spectra were recorded on Varian 640 instrument.

Research Results. Field tests are the most reliable method for determining the PM resistance to UV exposure. To reduce the experiment time, quick tests in a lab environment are used. The samples were subjected to photodegradation with a UV stabilizer ((1–4) compounds) and without it. In this case, the samples were affected by:

- the sun, a natural source of UV rays – within 365 days (field tests according to GOST 9.708-83);
- a xenon lamp, an artificial source of UV rays (flux density of UV radiation of 68 W/m^2 in the range of wavelengths of 300–400 nm, GOST 9.708-83) – for 504 hours.

It is known that in the process of photodegradation through IR-spectroscopy, the carbonyl and hydroxyl groups are accumulated in the PM samples [1, 12]. But the yield of hydroxyl groups is a few dozen times less than carbonyl groups[12], therefore, the rate and degree of the polymer degradation is determined by the concentration of carbonyl groups according to the respective absorption bands in the IR spectrum [10].

The analytical IR-spectroscopy application to the determination of the film oxidation rate is based on the difference in the spectra of the processed and not processed (check) samples. After UV irradiation, the absorption band of the carbonyl group at 1720 cm^{-1} (stretch vibrations of the carbonyl group are C = O) appears in the IR spectra of polyethylene (PE). This band is analytical for the quantitative analysis. At the maximum of the absorption band at 1720 cm^{-1}, the optical density value was determined by the baseline method. Calculations of the content of carbonyl groups in the samples were carried out by the well-known methods [10]. The research results are shown in Tables 1 and 2.

Table 1

Carbonyl groups content in polyethylene samples * treated with stabilizer solutions, under irradiation of xenon lamp, artificial ultraviolet source

No	Stabilizer solution concentration mol/l Stabilizer name	0.1 M	0.05 M	0.025 M
		Content of C = O groups, %		
1	3-carboxamido-2,2,5,5-tetramethyl-pyrrolin-1-oxyl (1)	—	—	0.02
2	4-acetylamino-2,2,6,6-tetramethyl-piperidine-1-oxyl (2)	—	—	0.025
3	2-methyl-4,6-di-tert-butylphenol (3)	0.10	0.25	0.40
4	2,4,6-tri-tert-amylphenol (4)	0.10	0.30	0.45
5	Check sample**	2.50	2.50	2.50

* No carbonyl groups were found in the sample before testing.

** Not treated with stabilizer solution.

Table 2

Carbonyl groups content in polyethylene samples* treated with stabilizer solutions, under irradiation of the sun, natural ultraviolet source (exposure period was 365 days)

No	Stabilizer solution concentration mol/l Stabilizer name	0.1 M	0.05 M	0.025 M
		Content of C = O groups, %		
1	3-carboxamido-2,2,5,5-tetramethyl-pyrrolin-1-oxyl (1)	—	—	0.016
2	4-acetylamino-2,2,6,6-tetramethyl-piperidine-1-oxyl (2)	—	—	0.021
3	2-methyl-4,6-di-tert-butylphenol (3)	0.07	0.095	0.16
4	2,4,6-tri-tert-amylphenol (4)	0.06	0.09	0.17
5	Check sample**	0.35	0.35	0.35

* No carbonyl groups were found in the sample before testing.

** Not treated with stabilizer solution.

The IR spectra analysis showed that the content of carbonyl groups in the check samples was significantly higher than in the treated samples. Fig. 1 shows the IR spectra of CS and the samples treated with 0.025 M solutions of stabilizers (2) and (4) after irradiation with an artificial ultraviolet source.

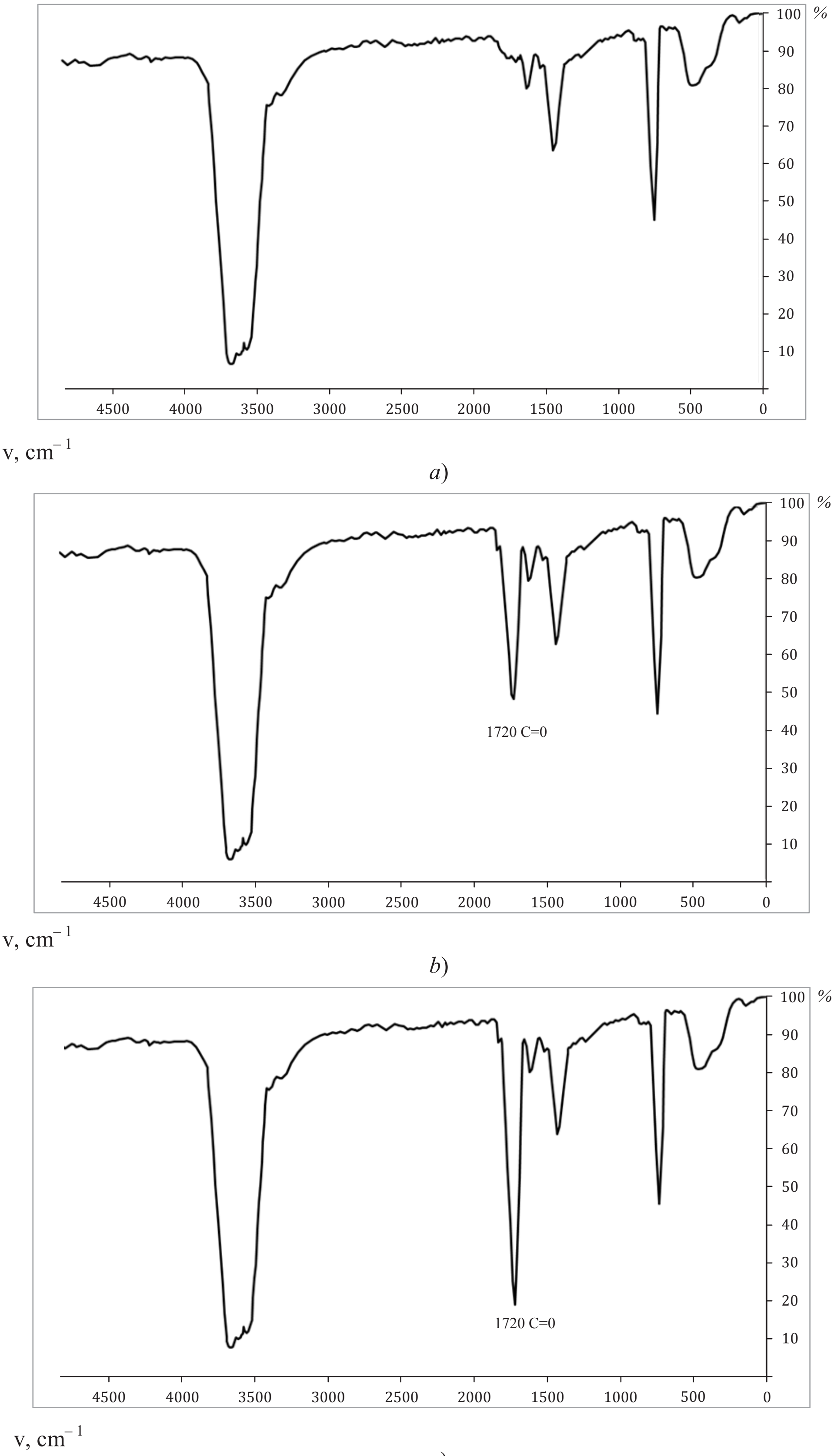

Fig. 1. IR spectra of PE-film samples: treated with 0.025 M solution of 4-acetylamino-2,2,6,6-tetramethylpiperidine-1-oxyl (2) (*a*); treated with 0.025 M solution of 2,4,6-tri-tert-amylphenol (4) (*b*); check sample (*c*). Absorption level is shown on the right vertical scale.

The onset of the degradation process in the sample treated with SHP (4) is characterized by the appearance of a low-intensity absorption band at 1720 cm^{-1} in the IR spectrum (Fig. 1, *b*). Such a band is practically absent in the sample treated with the stabilizer (2) from the NR series (Fig. 1, *a*). Consequently, the contribution of NR to the deceleration of photodecomposition processes is much higher than of the SHP.

UV radiation destroyed the CS. This is evidenced by the effect of accumulation of carbonyl groups in the sample manifested in an increase in the intensity of the absorption band at 1720 cm^{-1} (Fig. 1, *c)*.

Using IR spectroscopy, it was shown that UV-irradiation of PE films causes the accumulation of carbonyl groups associated with photodecomposition of PE carbon chains. Fig. 2 shows the kinetic curves of the accumulation of carbonyl groups during the simulated film photooxydation depending on the exposure time.

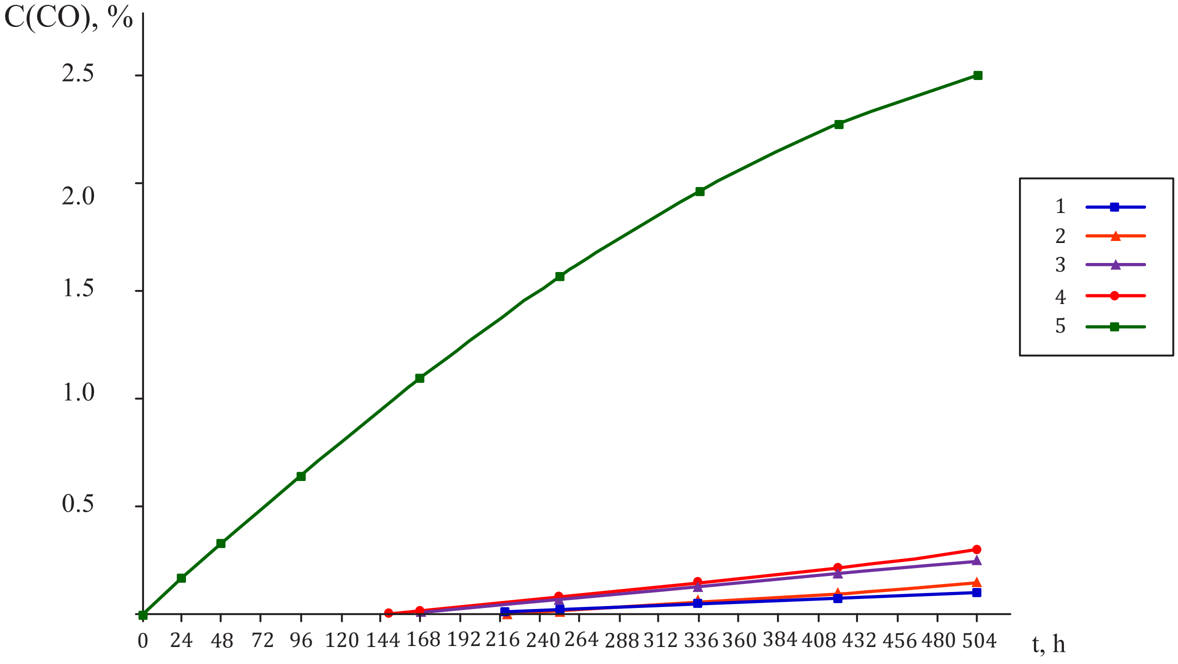

Fig. 2. Dependence of accumulation rate of carbonyl groups on time of simulated UV irradiation of samples treated with: 1 – 0.025 M solution of 3-carboxamido-2,2,5,5-tetramethylpyrrolin-1-oxyl; 2 – 0.025 M solution of 4-acetylamino-2,2,6,6-tetramethylpiperidine-1-oxyl; 3 – 0.025 M solution of 2-methyl-4,6-di-tert-butylphenol; 4 – 0.025 M solution of 2,4,6-tri-tert-amylphenol; 5 – check sample was not processed

The analysis of the data obtained shows that NR (1, 2) and SHP (3, 4) essentially slow down the photoinitiated oxidation destruction of PE and reduce the number of breaks of macromolecules. This is evidenced by the appearance of an induction period with an increase in the exposure time (see Fig. 2).

At the initial stage of the experiment, changes in CS are observed. Gradually, the concentration of carbonyl groups in the film not treated with a stabilizer increases. This is associated with an increase in the rate of oxidation processes causing the structure destruction of the PE carbon chains and the formation of low molecular weight active components (radical particles). In the PE samples treated with stabilizers (1-4), no changes are observed.

After about 150 hours, carbonyl groups are recorded in the samples treated with SHP (3, 4) solutions; after 220 hours – in the samples treated with NR solutions (1, 2). The accumulation rate of carbonyl groups increases linearly within 150–200 hours. Further, the dependence is maintained during the whole process of photo-oxidation (up to 504 hours).

The induction period in the presence of NR and SHP can be explained by the ability of stabilizers (1–4) to capture radicals quantitatively from the first moment; as a result, the process of destruction is inhibited at this stage. In this case, NR quickly interact with alkyl radicals, and, involving the polymer, they are converted into hydroxylamines capable of restoring radical particles [6, 7, 12]. SHP can turn into quinones or mono- and diesters of hydroquinones [6], which are also traps for radical particles.

The samples treated and not treated with stabilizers were also irradiated by a natural ultraviolet source according to GOST 9.708-83 for 365 days (see Table 2). The indicator of natural photo-oxidation of PE films was monitored after 1, 3, 6, 9, and 12 months (Fig. 3).

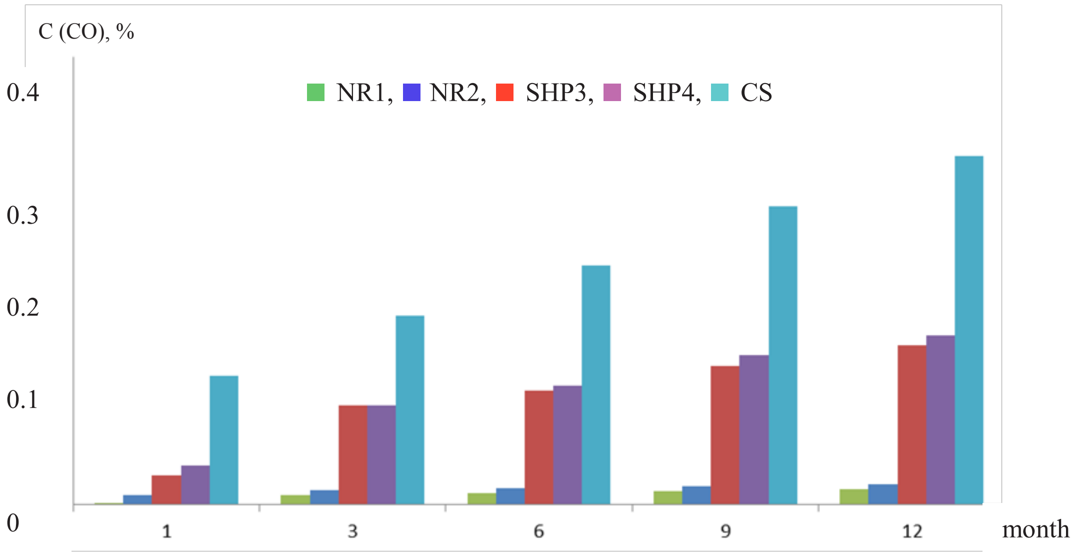

Fig. 3. Monitoring of indicator of concentration of carbonyl groups in PE film samples treated with 0.025 M stabilizer solution (1–4) and check sample (5)

Comparison of samples treated with NR (1, 2) and SHP (3, 4) shows the following: in the first case, the concentration of carbonyl groups increases insignificantly, in the second case, the content of carbonyl groups is sequence higher. In CS, a significant increase in the concentration of carbonyl groups was recorded after 1 month.

It should be also noted that in the course of testing of CS, PE films became brittle, and at the end of the experiment, they broke down, in contrast to the samples treated with stabilizer solutions.

Discussion and Conclusions. It is established that the best photo stabilizers of polyethylene are nitroxide radicals. Significant difference between the radicals of the 2,2,6,6-tetramethylpiperidine and 2,2,5,5-tetramethylpyrroline was not detected. Under the conditions of photodegradation, the SHP have a less stabilizing effect, yielding to nitroxide radicals.

The inhibitory effect of NR and SHP is associated with their ability to interact with radical particles formed as a result of the polymer photodegradation.

The tested compounds from NR class effectively slow down the process of photo-oxidation degradation and can be recommended for application as polymer stabilizers.

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