CHEMISTRY AND TECHNOLOGY OF ORGANIC SUBSTANCES

ХИМИЯ И ТЕХНОЛОГИЯ ОРГАНИЧЕСКИХ ВЕЩЕСТВ

ISSN 2686-7575 (Online)

https://doi.org/10.32362/2410-6593-2022-17-4-298-310

UDC 661.1 + 547.426

RESEARCH ARTICLE

Synthesis of stabilizers based on glycerides of monocarboxylic acids for industrial chloroparaffins

Yuriy L. Zotov✉, Daria M. Zapravdina, Evgeniy V. Shishkin, Yuriy V. Popov

Volgograd State Technical University, Volgograd, 400005 Russia
✉Corresponding author, e-mail: ylzotov@mail.ru

Abstract

Objectives. *The study aimed to develop new effective heat stabilizers based on glycerol esters of monocarboxylic acids for industrial chlorinated paraffins and to select of the optimal ratio of active ingredients in the stabilizing composition in order to provide the maximum thermostabilizing effect.*

Methods. *The thermostabilizing effect of the studied samples on chlorinated paraffins was evaluated according to the standard method for determining the thermal stability of liquid chlorinated paraffins in terms of the mass fraction of split off hydrogen chloride. Quantitative and qualitative analysis of the obtained mixtures of monocarboxylic acid glycerides was carried out using chromato-mass spectrometry.*

Results. *Glycerides of monocarboxylic acids (oleic, octanoic, hexanoic, and propionic acids) were obtained and identified, and the compositions of the resulting mixtures of mono-, di- and triesters were determined. The stabilizing effect of the obtained mixtures of glycerides of monocarboxylic acids in the amount of 0.5–2.0 wt parts per 100 wt parts of unstabilized industrial chlorinated paraffin CP-30 was determined. The combined use of glycerides of monocarboxylic acids with calcium-containing compounds as a complex stabilizer with a molar ratio of esters/Ca 0.93–0.86/0.07–0.14, respectively, was investigated. Chloroparaffin CP-470, stabilized by the developed complex stabilizer, was successfully used in a polyvinyl chloride composition for cable compound of the brand OM-40.*

Conclusions. *A proposed variant of a complex stabilizer for chlorinated paraffins based on Russian raw materials for import substitution will expand the range of effective stabilizers for organochlorine substances. Glycerides of monocarboxylic acids are shown to exhibit a thermostabilizing effect on industrial chlorinated paraffins. The relationship between the length of the hydrocarbon substituent of the carboxylic acid in the ester and the thermostabilizing effect is obtained. With an increase in the number of carbon atoms in the hydrocarbon substituent of the carboxylic acid, the heat-stabilizing ability decreases. The minimum sufficient concentration of glycerides of carboxylic acids was 0.05 ± 0.005 mol/kg, above which no increase in the thermostabilizing effect on chloroparaffin was observed. A synergistic ratio of the components of the stabilizing mixture in terms of thermal stability—glycerides of monocarboxylic acids/calcium-containing compounds—was found equal to 0.85–0.9/0.15–0.1.*

Keywords: *chloroparaffins, thermal stability, esterification, glycerol esters, calcium glyceroxide*

For citation: Zotov Yu.L., Zapravdina D.M., Shishkin E.V., Popov Yu.V. Synthesis of stabilizers based on glycerides of monocarboxylic acids for industrial chloroparaffins. *Tonk. Khim. Tekhnol. = Fine Chem. Technol*. 2022;17(4):298–310 (Russ., Eng.). https://doi.org/10.32362/2410-6593-2022-17-4-298-310

НАУЧНАЯ СТАТЬЯ

Синтез стабилизаторов на основе глицеридов монокарбоновых кислот для промышленных хлорпарафинов

Ю.Л. Зотов✉, Д.М. Заправдина, Е.В. Шишкин, Ю.В. Попов

Волгоградский государственный технический университет, Волгоград, 400005 Россия
✉Автор для переписки, e-mail: ylzotov@mail.ru

Аннотация

Цели. *Разработать новые эффективные термостабилизаторы на основе сложных эфиров глицерина монокарбоновых кислот для промышленных хлорпарафинов. Найти оптимальное соотношение действующих веществ стабилизирующей композиции обеспечивающее максимальное термостабилизирующее действие.*

Методы. *Оценку термостабилизирующего действия исследуемых образцов на хлорированные парафины проводили по стандартной методике определения термостабильности жидких хлорпарафинов в пересчете на массовую долю отщепленного хлористого водорода. Количественный и качественный анализ полученных смесей глицеридов монокарбоновых кислот проводили с использованием хромато-масс-спектрометрического анализа.*

Результаты. *Получены и идентифицированы глицериды монокарбоновых кислот (олеиновой, октановой, гексановой и пропионовой кислот), определены составы образующихся смесей моно-, ди- и триэфиров. Определено стабилизирующее действие полученных смесей глицеридов монокарбоновых кислот в количестве 0.5–2.0 мас. ч. на 100 мас. ч. нестабилизированного промышленного хлорпарафина марки ХП-30. Исследовано совместное использование глицеридов монокарбоновых кислот с кальцийсодержащими соединениями в качестве комплексного стабилизатора с мольным соотношением эфиры/Ca 0.93–0.86/0.07–0.14 соответственно. Хлорпарафин ХП-470, стабилизированный разработанным комплексным стабилизатором, успешно использован в поливинилхлоридной композиции для кабельного пластиката марки ОМ-40.*

Выводы. *Предложен вариант комплексного стабилизатора для хлорпарафинов на основе российского сырья для импортозамещения, расширяющий ассортимент эффективных стабилизаторов хлорорганических веществ. Установлено, что глицериды монокарбоновых кислот проявляют термостабилизирующее действие на промышленные хлорпарафины. Обнаружена взаимосвязь длины углеводородного заместителя карбоновой кислоты в сложном эфире на термостабилизирующее действие. С увеличением числа атомов углерода в углеводородном заместителе карбоновой кислоты термостабилизирующая способность снижается. Установлена минимальная достаточная концентрация глицеридов карбоновых кислот 0.05 ± 0.005 моль/кг, выше которой не наблюдается увеличение термостабилизирующего действия на хлорпарафин. Найдено синергическое соотношение компонентов стабилизирующей смеси по термостабильности: глицериды монокарбоновых кислот/кальцийсодержащие соединения, равное 0.85–0.9/0.15–0.1.*

Ключевые слова: *хлорпарафины, термостабильность, этерификация, сложные эфиры глицерина, глицерат кальция*

Для цитирования: Зотов Ю.Л., Заправдина Д.М., Шишкин Е.В., Попов Ю.В. Синтез стабилизаторов на основе глицеридов монокарбоновых кислот для промышленных хлорпарафинов. *Тонкие химические технологии*. 2022;17(4):298–310. https://doi.org/10.32362/2410-6593-2022-17-4-298-310

INTRODUCTION

Representing multi-tonnage products of the organic synthesis industry, chlorinated paraffins are used as secondary plasticizers for polymer compositions based on polyvinyl chloride (PVC) to partially replace primary plasticizers such as phthalates and phosphate esters. The use of chlorinated paraffins makes it possible to increase the fire resistance and low-temperature strength of polymer products [1]. Chloroparaffins are widely used in the production of cable materials, wall panels, shoe plastic, and other products. However, chloroparaffins are subject to thermal decomposition. Technological temperatures of polyvinyl chloride processing exceed 200°C, leading to the decomposition of chloroparaffins, along with the release of gaseous hydrogen chloride, which is known [2] to initiate of the process of dehydrochlorination of organochlorine compounds.

To prevent the process of thermal degradation of chloroparaffins, which are part of the PVC composition, the use of stabilizers is required to increase its own thermal stability. Chloroparaffins are traditionally stabilized with epoxy compounds, such as epoxidized soybean oil or epoxidized resins (ED-20) [3, 4]. For example, mixtures containing piperidine derivatives with phosphoric esters [5], aliphatic ketone with benzylamine, aliphatic amine, or amino alcohol [6], phosphoric acid esters with glycerol [7], adamantyl-containing imidic acid derivatives with epoxidized soybean oil [8] are used as stabilizers. Hydrogen chloride acceptors are also used as heat stabilizers, for example, salts of aliphatic carboxylic acids with the number of carbon atoms in the chain C_{10}–C_{23} and alkaline earth metal of group II of the Periodic Table [9, 10]. Thus, a more pronounced thermostabilizing effect is achieved, both due to the well-known synergistic effect [11] and chemical processes occurring during thermal stabilization at different speeds and with different sequences of reaction of different salts.

The development of technologies for the production of biodiesel by transesterification of

vegetable oils with methanol (or other alcohols) has led to the appearance on the market of a significant quantity of glycerol, which is formed as a byproduct [12]. In this regard, the use of glycerol as a cheap Russian renewable and environmentally friendly raw material for the production of products with high added value has become relevant.

In order to improve the quality of industrial chlorinated paraffins, we are developing new complex stabilizers based on glycerol esters and calcium-containing compounds, which will not only increase the thermal stability of the initial chloroparaffin, but also favorably affect the physicomechanical properties of the polymer composition and finished products. Since there is no information in the scientific and technical literature about the stabilizing effect of carboxylic acid glycerides on chlorinated hydrocarbons, research in this direction is of practical and scientific interest.

MATERIALS AND METHODS

Glycerol (98.5 wt %, c.p.), oleic acid of the B-115 brand (97.4 wt %, tech.), octane acid (99.5 wt %, c.p.), hexanoic acid (99 wt %, c.p.), propionic acid (99 wt %, c.p.), calcium hydroxide (97 wt %, p.a., used after calcination at 300°C for 30 min), petroleum toluene (99 wt %, p.a.), chloroparaffin CP-30 grade A (STO 00203275-201-2006[1] with amendments 1, 2) (manufactured by *Chimmed* and *Kaustik*, Russia) were used in the work. To conduct studies of the thermostabilizing effect of monocarboxylic acid glycerides on organochlorine compounds, chloroparaffin CP-30 was specially synthesized in production conditions and sampled after the end of the hydrogen chloride blowing stage before the mixing operation with a prescription stabilizer.

Identification of the product obtained by esterification of glycerol with carboxylic acids was carried out using chromato-mass spectrometric analysis on a Saturn 2100T chromato-mass spectrometer (*Varian*, USA) with a quartz capillary column VF-1ms 30 M × 0.25 mm × 0.25 μm and the following parameters: carrier gas—helium; flow rate—1.2 mL/min; injector with a 1:10 flow split; injector temperature—280°C. When programming the temperature of the capillary column, the following parameters were used: initial temperature—80°C; isotherm time—3 min; final temperature—300°C, isotherm time—2 min; heating rate—10°C/min; total analysis time—30 min. The detector is mass selective with electron ionization energy of 70 eV. The spectra were recorded in full scan mode (SCAN) within the mass range from 40 to 650 Da at a data collection rate of 2000 Da/s.

Oleic acid monoglyceride: mass spectrum, *m*/*z* (I_{rel}, %): 356 (3.2) $[M]^+$, 339 (23.7), 264 (99.9), 166 (15.7), 137 (24.9), 112 (23.3), 98 (45.9), 83 (31.8), 69 (32.4), 55 (60.3), 41 (55.7). **Oleic acid diglyceride:** mass spectrum, *m*/*z* (I_{rel}, %): 339 (11.8), 265 (8.6), 185 (51.2), 129 (99.9), 97 (14.3), 83 (21.4), 69 (28.2), 55 (59.1), 41 (42.4). **Oleic acid:** mass spectrum, *m*/*z* (I_{rel}, %): 282 (5.5) $[M]^+$, 264 (41.9), 151 (18.9), 123 (24), 111 (30.3), 97 (65), 83 (67.8), 69 (66.4), 55 (99.9), 41 (80).

Octanoic acid monoglyceride: mass spectrum, *m*/*z* (I_{rel}, %): 218 (17.3) $[M]^+$, 201 (100), 127 (62.5), 57 (74.9). **Octanoic acid diglyceride:** mass spectrum, *m*/*z* (I_{rel}, %): 327 (67.2), 242 (18.2), 201 (100), 127 (83.2), 57 (75.3). **Octanoic acid triglyceride:** mass spectrum, *m*/*z* (I_{rel}, %): 327 (100), 313 (12.2), 242 (17.5), 201 (25.4), 127 (71.5), 57 (57.8). **Octanoic acid:** mass spectrum, *m*/*z* (I_{rel}, %): 144 (13.6) $[M]^+$, 126 (10.2), 114 (18.6), 100 (53.2), 73 (75), 60 (100), 55 (58.1), 43 (52.6).

Hexanoic acid monoglyceride: mass spectrum, *m*/*z* (I_{rel}, %): 190 (23.5) $[M]^+$, 172 (99.9), 99 (87.3), 71 (49.8), 43 (100). **Hexanoic acid diglyceride:** mass spectrum, *m*/*z* (I_{rel}, %): 271 (99.9), 173 (29.9), 99 (10.3), 43 (13.8). **Hexanoic acid triglyceride:** mass spectrum, *m*/*z* (I_{rel}, %): 271 (7.4), 227 (7.5), 100 (6.7), 99 (99.9), 71 (20.6), 43 (22.8). **Hexanoic acid:** mass spectrum, *m*/*z* (I_{rel}, %): 116 (0.9) $[M]^+$, 87 (13.4), 73 (44.5), 60 (100), 41 (19.6).

Propionic acid monoglyceride: mass spectrum, *m*/*z* (I_{rel}, %): 117 (12.7) $[M]^+$, 88 (7.2), 61 (14.5), 57 (100). **Propionic acid diglyceride:** mass spectrum, *m*/*z* (I_{rel}, %): 187 (5.1), 148 (33.9), 131 (99.9), 117 (13.7), 57 (51.6). **Propionic acid triglyceride:** mass spectrum, *m*/*z* (I_{rel}, %): 187 (5.7), 173 (17.5), 121 (8.1), 117 (14.3), 57 (100). **Propionic acid:** mass spectrum, *m*/*z* (I_{rel}, %): 74 (100) $[M]^+$, 57 (46.7), 45 (89.3).

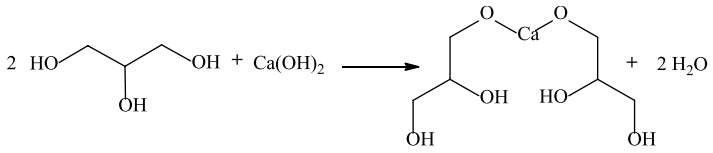
The infrared (IR) spectra of the obtained calcium glyceroxide were recorded in air at room temperature on a Nicolet-6700 IR Fourier spectrometer (*Thermos Scientific*, USA) in the region of 400–4000 cm^{-1} with a scanning step of 0.5 cm^{-1}.

The elemental analysis was performed using the Elementar Vario EL cube analyzer (*Abacus Analytical Systems GmbH*, Germany).

[1] https://www.kaustik.ru/ru/index.php/produktsiya-i-uslugi/khlorparafiny/khlorparafin-khp-30, accessed March 25, 2022.

Preparation of the catalyst

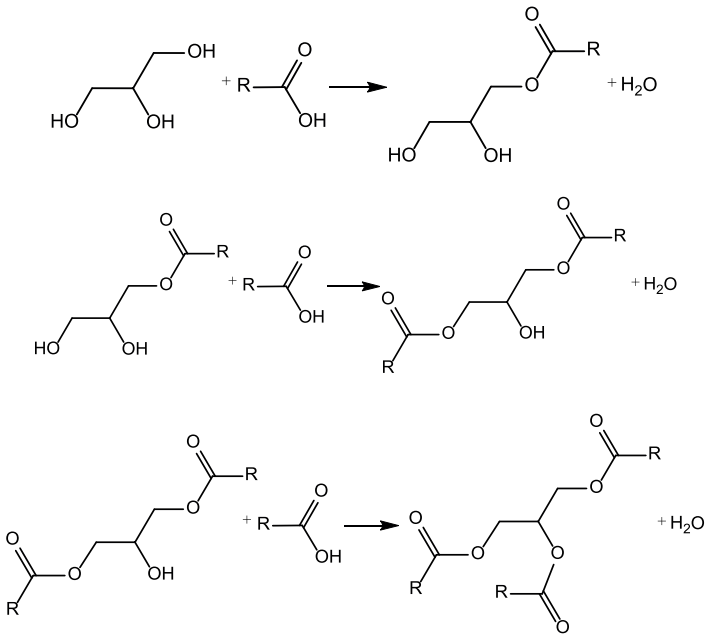
The synthesis of calcium glyceroxide [13] was carried out by the interaction of glycerol with calcium hydroxide (Scheme 1). For removing reaction water by azeotropic distillation using a reflux condenser and an upper-drive agitator, 1.36 mol of glycerol, 0.22 mol of calcium hydroxide, and 30 mL of toluene as an azeotropic forming agent were loaded into the reactor equipped with a Dean-Stark nozzle. The reaction mass was stirred at 450 ± 10 rpm and boiled with the withdrawal of reaction water in the Dean-Stark nozzle. After distilling the calculated amount of reaction water (duration about 7 h), the reaction mass was cooled. The resulting precipitate was separated by filtration under vacuum, washed with ethanol until the unreacted glycerol was completely removed, and dried for 1 h at a temperature of 105°C. The resulting calcium glyceroxide was stored in a desiccator under argon over solid NaOH. IR spectrum, ν, cm^{-1}: 3229 w (OH), 2874 m (C–H), 2836 w (C–H), 1128 w (C–O), 1091 m (C–O), 3641 (Ca–O), 1370 w [δ(S–O–N)], 1306 s [δ(C–O–N)]. Elemental analysis: found with (29.9 ± 3.0%), H (6.0 ± 0.6%) [$Ca(C_3H_7O_3)_2$]; calculated with (32.4%), H (6.3%).



Scheme 1. Synthesis of calcium glyceroxide.

Esterification of glycerol with monocarboxylic acids

The interaction of glycerol with carboxylic acids (Scheme 2) was carried out in a three-necked flask equipped with a reflux condenser, a Dean-Stark nozzle for removing reaction water by azeotropic distillation, a thermometer and an upper-drive agitator. Glycerol, calcium glyceroxide, monocarboxylic acid and toluene as an azeotroping agent were loaded into the reactor (Table 1). Then the temperature of the reaction mass was gradually increased until the azeotrope began to boil (85–110°C) and kept at this temperature for 10 h. As the reaction progressed, the resulting reaction water was distilled with azeotrope and toluene. After distilling water in an amount of approximately 1 mol, toluene was distilled from the reaction mass in the vacuum of a water jet pump at a temperature of 110°C for 1 h. The unreacted glycerol was separated on the dividing funnel.



R: $C_{17}H_{33}$, C_7H_{15}, C_5H_{11}, C_2H_5.

Scheme 2. Interaction of glycerol with carboxylic acids.

Method of isolation of glycerides of monocarboxylic acids

Following the esterification process, the reaction mass was mixed with acetone in a mass ratio of 1:1. The resulting mixture was loaded into the reactor and a few drops of phenolphthalein alcohol solution were added. Then, with stirring, a 0.1 mol/dm^3 sodium hydroxide solution was added dropwise to a stable weak pink color over more than 30 s. The resulting precipitate was separated by centrifugation. Then acetone was distilled from the centrifuge at atmospheric pressure.

Investigation of the thermal stability of chloroparaffins

The effectiveness of the obtained samples as complex stabilizers was evaluated according to the standard method for determining the thermal stability of liquid chloroparaffins in terms of the mass fraction of separated hydrogen chloride.

As model compositions, a mixture of the following composition was selected to test the stabilizing effect of additives: 100 wt parts of unstabilized chloroparaffin of the CP-30 brand and 0.5–2 wt parts of the tested additive.

The analyzed mixture in the amount of 9.5–10.5 g was loaded into a test tube equipped

[2] STO 00203275-201-2006 with amend. 1, 2.

Table 1. Loading of reagents for obtaining complex stabilizers

Sample No.	Starting reagents			
	Glycerol, mol	Carboxylic acid		Calcium glyceroxide, mol
		Name	Quantity, mol	
1*	1	Oleic	1	0.015
2*	1	Octane	1	0.015
3*	1	Hexane	1	0.015
4*	1	Propionic	1	0.015
6	1	Oleic	1.13	0.066
7	1	Oleic	1.21	0.104
8	1	Oleic	1.30	1.148
9	1	Octanoic acid	1.30	1.148
10	1	Hexane	1.30	1.148
11	1	Propionic	1.30	1.148

*Glycerides of monocarboxylic acids were isolated from the resulting reaction mixture according to the procedure.

with a nozzle for nitrogen injection. The test tube was connected to the nitrogen supply line. The exhaust pipe of the nozzle was connected to two sequentially connected Drexel flasks, into the second of which 100 mL of distilled water was pre-poured. The test tube with the analyzed mixture was placed in a bath filled with a thermostatic liquid, preheated to 175 ± 2°C and nitrogen was supplied through a rheometer at a speed of 30 cm^3/min. After holding the test tube for 4 h, the Drexel flask containing water was disconnected. The resulting aqueous solution was titrated with a solution of sodium hydroxide of molar concentration $C_{(NaOH)}$ = 0.01 mol/dm^3 until the color change of the indicator.

Thermal stability was calculated in terms of the mass fraction of separated HCl (X) as a percentage using the formula

$$X = (V \times 0.0003646 \times 100 \times K)/m,$$

where V is the volume of sodium hydroxide solution of molar concentration $C_{(NaOH)}$ = 0.01 mol/dm^3 spent on titration, cm^3; 0.0003646 g/cm^3 is HCl mass corresponding to 1 cm^3 of sodium hydroxide solution of molar concentration $C_{(NaOH)}$ = 0.01 mol/dm^3; m is the mass of the analyzed sample, g; K is the coefficient of correction to the sodium hydroxide solution.

RESULTS AND DISCUSSION

Glycerol esters and monocarboxylic acids were selected as heat stabilizers for industrial chlorinated paraffins.

A method developed [14] for esterification of glycerol with monocarboxylic acids in the presence of calcium glyceroxide as a catalyst can be used to obtain glycerol esters without the formation of byproducts characteristic of acid catalysis. This process can be described by

successive reactions with the formation of the following products: monoglyceride, diglyceride, and triglyceride.

Glycerides of carboxylic acids synthesized according to the proposed method using monocarboxylic acids with different hydrocarbon substituent lengths were identified by chromato-mass spectrometric analysis. The compositions of the obtained mixtures of glycerides are presented in Table 2.

The resulting mixtures of glycerides were tested as heat stabilizers of liquid chloroparaffins. The assessment of the thermostabilizing effect of the studied compounds was carried out by determining the thermal stability in terms of the mass fraction of separated hydrogen chloride. For unstabilized chloroparaffin CP-30 (control sample), the mass fraction of the separated hydrogen chloride of 0.714% was measured according to the above-described method.

The results of the study of the thermostabilizing effect of the studied mixtures of glycerides of monocarboxylic acids on chloroparaffin are presented in Figs. 1 and 2.

The results obtained indicate a high thermal stability value even with a small quantity of glycerides. Thus, with a content of 0.5 wt parts glycerides of oleic acid (sample 1) per 100 wt parts of unstabilized chloroparaffin, a mass fraction of separated hydrogen chloride of about 0.07% is achieved, which is 10 times lower than unstabilized chloroparaffin.

According to the graphs of the dependence of the mass fraction of separated hydrogen chloride on the content of carboxylic acid glycerides obtained after converting the weight parts to a molal concentration (Fig. 2), an increase in the stabilizer concentration of more than 0.05 mol/kg does not lead to an increase in thermal stability.

The following conclusions can be drawn on the basis of the data analysis:

– the stabilizing effect of glycerides of carboxylic acids on industrial chloroparaffin was established. It was found that propionic acid glycerides have the most effective thermostabilizing effect;

– the relationship between the length of the hydrocarbon substituent of carboxylic acid in a ester and the thermostabilizing effect was obtained. It was shown that stabilizing ability decreases with an increase in the number of carbon atoms in the hydrocarbon substituent of carboxylic acid;

– the concentration of glycerides of carboxylic acids at which the maximum thermostabilizing ability is achieved was established. It is advisable to study additives consisting of mixtures of glycerides of various carboxylic acids at a concentration of 0.05 ± 0.005 mol/kg in order to study synergy.

Calcium compounds are standard stabilizers for organochlorine compounds [11]. According to the method developed by us [14], glycerides of carboxylic acids can be synthesized using calcium glyceroxide as a catalyst. During synthesis, calcium glyceroxide is converted into calcium carboxylate (Scheme 3) in the presence of an excess of carboxylic acid corresponding to the amount of catalyst to obtain a complex stabilizer containing glycerides of carboxylic acids and calcium-containing compounds as active substances.

Calcium salts are effective acceptors of hydrogen chloride; when used as part of a stabilizing additive, they neutralize hydrogen chloride to

Table 2. Compositions of the studied mixtures of glycerides of carboxylic acids

Sample No.	Carboxylic acid glycerides	Amount, wt %		
		MG	DG	TG
1	Oleic acid glycerides	81.8	18.2	–
2	Octanoic acid glycerides	68.4	30.4	1.2
3	Hexanoic acid glycerides	66.8	30.7	2.5
4	Propionic acid glycerides	67.5	29.4	3.1

Note: MG are monoglycerides; DG are diglycerides; TG are triglycerides.

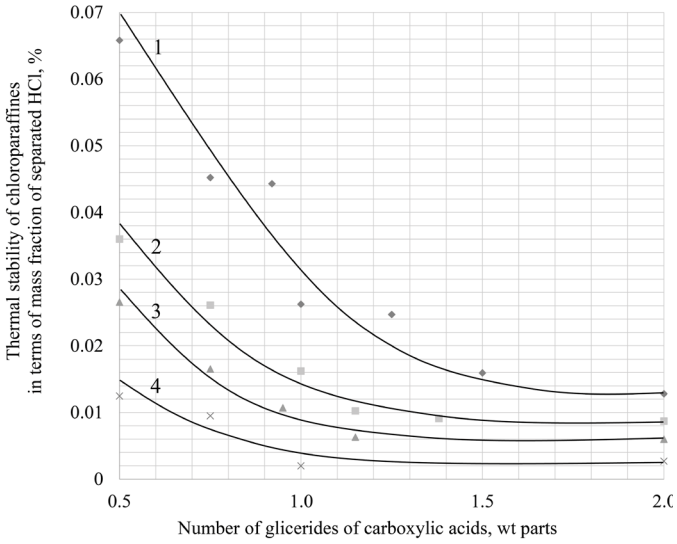


Fig. 1. Dependence of the mass fraction of cleaved hydrogen chloride for chlorpapafin CP-30 on the content of carboxylic acid glycerides (wt parts).
♦ Oleic acid glycerides;
■ Octanoic acid glycerides;
▲ Hexanoic acid glycerides;
× Propionic acid glycerides.

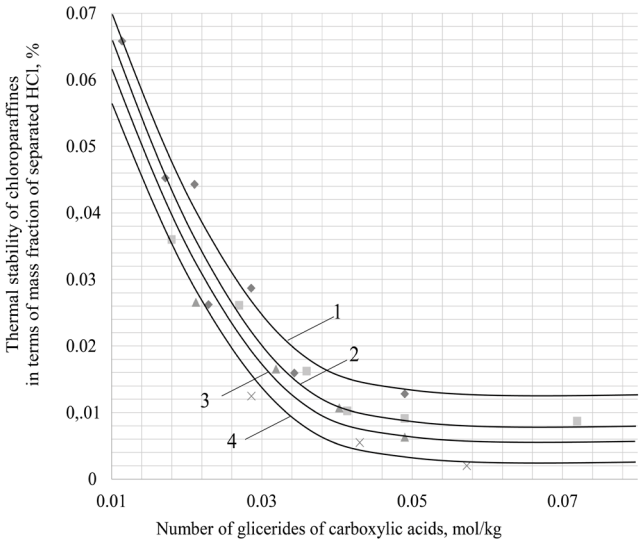


Fig. 2. Dependence of the mass fraction of cleaved hydrogen chloride for chlorpapafin CP-30 on the content of carboxylic acid glycerides (mol/kg).
♦ Oleic acid glycerides;
■ Octanoic acid glycerides;
▲ Hexanoic acid glycerides;
× Propionic acid glycerides.

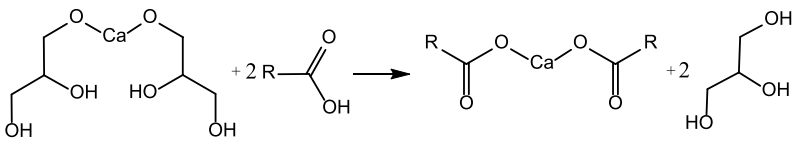
prevent its catalytic effect on the reaction of dehydrochlorination of chloroparaffin. It has been assumed that the combined use of monocarboxylic acid glycerides with calcium-containing compounds could lead to a synergistic effect. To determine the ratio of the components of the synergetic composition, laboratory samples (6–8) with different molar ratios of active substances were prepared. Compositions obtained using oleic acid were selected as the object of research. The molar ratios of active substances and the results of thermal stability are presented in Table 3.

Model compositions for testing the stabilizing effect of the studied additives contain: 100 wt parts of unstabilized chloroparaffin of the CP-30 brand and 2 wt parts of the tested samples (1, 5–11).

The obtained results were compared with the thermostabilizing effect of individual components of the tested compositions: oleic acid glycerides (sample 1) and calcium oleate (sample 5).

The analysis of the obtained results supports the conclusion that oleic acid glycerides exhibit a synergistic effect on thermal stability in combination with calcium-containing compounds (samples 7 and 8). This phenomenon is explained by the combined action of the used substances acting on various stabilization mechanisms. The resulting hydrogen chloride is chemically bound by calcium compounds. When chloroparaffins are stabilized, carboxylic acid glycerides stabilize labile chlorine atoms due to the dipole interaction between chlorine atoms in chloroparaffin and carbonyl groups of esters.

In accordance with the found synergistic ratio of the components of the stabilizing composition, laboratory samples (8–11) synthesized using monocarboxylic acids with different lengths of the hydrocarbon substituent were



Scheme 3. Conversion of calcium glyceroxide to calcium carboxylate.

Table 3. Influence of the molar ratio of the active substances of the stabilizing mixture on the thermal stability of chlorinated paraffin CP-30

Sample No.	Ratio of the components of the stabilizing compositions, mol		Thermal stability of chlorinated paraffin in terms of the mass fraction of split off HCl, %
	Oleic acid glycerides	Ca^{2+}	
1	1	–	0.0128
6	0.93	0.07	0.0093
7	0.90	0.10	0.0079
8	0.86	0.14	0.0042
5*	–	1	0.0085

*Calcium oleate was used to study the thermostabilizing effect of calcium-containing compounds.

prepared and tested. The obtained results of thermal stability of liquid chloroparaffin CP-30 are presented in Table 4 in terms of the mass fraction of separated hydrogen chloride.

Using the developed version of the complex stabilizer (sample 10), a stabilized sample of chloroparaffin of the CP-470 brand was subsequently used in the manufacture of OM-40 cable plastic according to the production recipe. Table 5 presents the physical and mechanical parameters of the obtained PVC plastics.

The manufacture and testing of cable plastic was carried out in the *Kaustik* specialized laboratory (Volgograd, Russia) in accordance with the requirements of STO 22542799-04-2001, amend. 1, 2, to OM-40. The test results showed that

Table 4. Thermal stability of CP-30 chlorinated paraffin in terms of the mass fraction of cleaved hydrogen chloride for synergistic mixtures of active ingredients

Sample No.	Used carboxylic acid in the preparation of stabilizing compositions	Ratio of components of stabilizing compositions, mol		Thermal stability of chlorinated paraffin in terms of the mass fraction of split off HCl, %
		Oleic acid glycerides	Ca^{2+}	
8	Oleic acid	0.860	0.140	0.0042
9	Octanoic acid	0.864	0.136	0.0033
10	Hexanoic acid	0.866	0.134	<0.0027
11	Propionic acid	0.870	0.130	<0.0027

Table 5. Physicomechanical properties of cable plastic compound grade OM-40

Normalized indicators of cable compound	Requirements of STO 22542799-04-2001, amend. 1, 2, to OM-40	Actual indicators	
		Plastic compound is made using chlorinated paraffin CP-470A produced by *Kaustik* (control)	Plastic compound is made using chlorinated paraffin CP-470 stabilized by the proposed composition
Breaking strength, kgf/cm^2, not less	122.4	148	144
Elongation at break, %, not less	300	546	523
Specific volume electrical resistance, Ω·m cm, not less	$1 \cdot 10^{11}$	$8.3 \cdot 10^{12}$	$5.16 \cdot 10^{12}$
Shore hardness, scale units	70–85	74 ± 2	75 ± 2
Density, g/cm^3, no more	1.45	1.41	1.41
Additional indicators			
Melt flow index of plastic compound granules at 185°C, 5 kgf, g/10 min[3]	Non-standardized	17.53	19.52
Thermal stability of plastic compound granules at 200°C, Congo red, min[4]	Non-standardized	100	110

the developed version of the stabilizer can be used to stabilize industrial chloroparaffins while maintaining the operational properties of the final products.

CONCLUSIONS

A variant of a complex stabilizer for chloroparaffins based on Russian raw materials for import substitution was proposed, expanding the range of effective stabilizers of organochlorine substances. It has been established that glycerides of monocarboxylic acids exhibit a thermostabilizing effect on industrial chloroparaffins. The relationship of the length of the hydrocarbon substituent of carboxylic acid in the ester to the thermostabilizing effect was obtained. With an increase in the number of carbon atoms in the hydrocarbon substituent of carboxylic acid, the thermostabilizing ability decreases. The minimum sufficient concentration of glycerides of carboxylic acids 0.05 ± 0.005 mol/kg was established. Above this concentration, there is no increase in the thermal stabilizing effect on chloroparaffin. A synergistic ratio of the components of the stabilizing mixture in terms of thermal

[3] GOST 11645-73. Plastics. Determination of flow index of thermoplastics melt by extrusion plastometer. Moscow: Izd. Standartov; 1994 (in Russ).

[4] GOST 14041-91. Plastics. Determination of the tendency of compounds and products based on vinyl chloride homopolymers and copolymers to evolve hydrogen chloride and any other acidic products of elevated temperatures. Congo red method. Moscow: Izd. Standartov; 1992 (in Russ).

stability was obtained as follows: glycerides of monocarboxylic acids/calcium-containing compounds, equal to 0.85–0.9/0.15–0.1. The tests of the developed sample of the complex stabilizer carried out in the *Kaustik* specialized laboratory demonstrated the possibility of its use for the stabilization of commercial chloroparaffins.

Acknowledgments

The work was performed using the equipment of the Center for Collective Use "Physicochemical methods of Analysis" at the Volgograd State Technical University. The authors thank the specialists of Kaustik, Volgograd, for investigating a complex stabilizer for industrial chloroparaffins.

Authors' contributions

Yu.L. Zotov – research concept, development of the experiment, discussion and analysis of the results, and writing the text of the article;

D.M. Zapravdina – research concept, planning and conducting experimental studies, processing the data obtained, and preparation of the data obtained for publication;

E.V. Shishkin – consultation on conducting individual stages of the study, scientific editing;

Yu.V. Popov – consultation on conducting individual stages of the study, scientific editing.

The authors declare no conflicts of interest.

REFERENCES

1. Zotov Yu.L., Butakova N.A., Popov Yu.V. *Okislenie promyshlennykh khlorparafinov kislorodom vozdukha* (*Oxidation of industrial chlorinated paraffins with atmospheric oxygen*). Volgograd: IUNL VolgGTU; 2014. 124 p. (in Russ.).

2. Oshin L.A., Treger Yu.A., Motsarev G.V., Sonin E.V., Sergeev E.V., Skibinskaya M.B., Gol'fand E.A. *Promyshlennye khlororganicheskie produkty*: *spravochnik* (*Industrial organochlorine products: handbook*). Moscow: Khimiya; 1978. 656 p. (in Russ.).

3. Rysaev U.Sh., Nafikov A.B., Gil'mutdinov A.T., Nafikova R.F., Rysaev V.U. Synergistic stabilizing compositions for chlorine-containing hydrocarbons. *Bashkirskii khimicheskii zhurnal = Bashkir Chemical Journal.* 2007;14(4):32–36 (in Russ.).

4. Klichkov I.S., Krishtal' N.F., Nakhimovich M.L., Poselenov A.I., Levanovich V.S., Kharitonov V.I. *Method of stabilization of trichlorethylene and perchlorethylene*: USSR Pat. 680303. Publ. 27.12.1999 (in Russ.).

5. Tsuyoshi M., Takushi A., Hirota S. *Method for stabilizing chlorinated aliphatic hydrocarbon*: JP Pat. 2009046444. Prior publ. data 22.08.2007; date of patent 05.03.2009.

6. Krishtal' N.F., Klichkov I.S. Nakhimovich M.L., Poselenov A.I., Sankov B.G., Sveshnikov A.V., Velichko I.N., Gerasimov F.E. *Method for stabilizing methylene chloride*: USSR Pat. 1387349. Publ. 27.06.2000 (in Russ.).

7. Rasulev Z.G., Krishtal' N.F., Nakhimovich M.L., Abdrashitov Ya.M., Rakhimov R.R., Islamshin A.Z. *Method of stabilizing 1,2-dichloroethane or 1,2,3-trichloropropane*: USSR Pat. 1555321. Publ. 07.04.1990 (in Russ.).

8. No B.I., Zotov Yu.L., Klimov D.S., Shishkin E.V., Klimov S.A., Shatalin Yu.V., Knyazeva E.A. Multifunctional compositions "SINSTAD" for polymers. XVII. Adamantyl derivatives of imic acids as stabilizers of chlorinated paraffins. *Plasticheskie massy*. 2004;(2):40–41 (in Russ.).

СПИСОК ЛИТЕРАТУРЫ

1. Зотов Ю.Л., Бутакова Н.А., Попов Ю.В. *Окисление промышленных хлорпарафинов кислородом воздуха*. Волгоград: ИУНЛ ВолгГТУ; 2014. 124 с.

2. Ошин Л.А., Трегер Ю.А., Моцарев Г.В., Сонин Э.В., Сергеев Е.В., Скибинская М.Б., Гольфанд Е.А. *Промышленные хлорорганические продукты: справочник*. М.: Химия; 1978. 656 с.

3. Рысаев У.Ш., Нафиков А.Б., Гильмутдинов А.Т., Нафикова Р.Ф., Рысаев В.У. Синергические стабилизирующие композиции для хлорсодержащих углеводородов. *Башкирский химический журнал*. 2007;14(4):32–36.

4. Кличков И.С., Кришталь Н.Ф., Нахимович М.Л., Поселенов А.И., Левanович В.С., Харитонов В.И. *Способ стабилизации трихлорэтилена и перхлорэтилена*: пат. 680303 СССР. Заявка № 2607154/04, заявл. 18.04.1978; опубл. 27.12.1999.

5. Tsuyoshi M., Takushi A., Hirota S. *Method for stabilizing chlorinated aliphatic hydrocarbon:* JP Pat. 2009046444. Prior publ. data 22.08.2007; date of patent 05.03.2009.

6. Кришталь Н.Ф., Кличков И.С. Нахимович М.Л., Поселенов А.И., Санков Б.Г., Свешников А.В., Величко И.Н., Герасимов Ф.Е. *Способ стабилизации метиленхлорида*: пат. 1387349 СССР. Заявка № 4098828/04, заявл. 28.07.1986; опубл. 27.06.2000.

7. Расулев З.Г., Кришталь Н.Ф., Нахимович М.Л., Абдрашитов Я.М., Рахимов Р.Р., Исламшин А.З. *Способ стабилизации 1,2-дихлорэтана или 1,2,3-трихлорпропана:* пат. 1555321 СССР. Заявка № 4207872/23-04, заявл. 06.03.1987; опубл. 07.04.1990, Бюл. № 13.

8. Но Б.И., Зотов Ю.Л., Климов Д.С., Шишкин Е.В., Климов С.А., Шаталин Ю.В., Князева Е.А. Многофункциональные композиции «СИНСТАД» для полимеров. XVII. Адамантилсодержащие производные имидовых кислот в качестве стабилизаторов хлорпарафинов. *Пластические массы*. 2004;(2):40–41.

9. Kutyanin L.I., Kuznetsov A.A., Poddubnyi I.S., Ivanova N.A., Sergeev S.A. *Method for stabilizing halogenated paraffins*: RF Pat. 2245318. Publ. 27.01.2005.

10. No B.I., Zotov Yu.L., Shipaeva T.A., Klimov D.S. Multifunctional compositions "SINSTAD" for polymers. II. Stabilization of chlorinated paraffins KhP-30 with metal stearates. *Plasticheskie massy*. 1997;(4):41–42 (in Russ.).

11. Minsker K.S., Fedoseeva G.T. *Destruktsiya i stabilizatsiya polivinilkhlorida* (*Destruction and stabilization of polyvinyl chloride*). Moscow: Khimiya; 1979. 272 p. (in Russ.).

12. Quispe C.A.G., Coronado C.J.R., Carvalho J.A. Glycerol: Production, consumption, prices, characterization and new trends in combustion. *Renewable and Sustainable Energy Reviews.* 2013;27:475–493. https://doi.org/10.1016/j.rser.2013.06.017

13. León-Reina L., Cabeza Au., Rius J., Maireles-Torres P., Alba-Rubio A.C., Granados M.L. Structural and surface study of calcium glyceroxide, an active phase for biodiesel production under heterogeneous catalysis. *J. Catal*. 2013;300:30–36. http://dx.doi.org/10.1016/j.jcat.2012.12.016

14. Zotov Yu.L., Zapravdina D.M. *Method for obtaining plasticiser for polyvinyl chloride composition*: RF Pat. 2643996. Publ. 06.02.2018.

9. Кутянин Л.И., Кузнецов А.А., Поддубный И.С., Иванова Н.А., Сергеев С.А. *Способ стабилизации галогенированных парафинов*: пат. 2245318 РФ. Заявка № 2002122154/04, заявл. 14.08.2002; опубл. 27.01.2005, Бюл. № 3.

10. Но Б.И., Зотов Ю.Л., Шипаева Т.А., Климов Д.С. Многофункциональные композиции «СИНСТАД» для полимеров. II. Стабилизация хлорпарафинов ХП-30 стеаратами металлов. *Пластические массы*. 1997;(4):41–42.

11. Минскер К.С., Федосеева Г.Т. *Деструкция и стабилизация поливинилхлорида*. М.: Химия; 1979. 272 с.

12. Quispe C.A.G., Coronado C.J.R., Carvalho J.A. Glycerol: Production, consumption, prices, characterization and new trends in combustion. *Renewable and Sustainable Energy Reviews.* 2013;27:475–493. https://doi.org/10.1016/j.rser.2013.06.017

13. León-Reina L., Cabeza Au., Rius J., Maireles-Torres P., Alba-Rubio A.C., Granados M.L. Structural and surface study of calcium glyceroxide, an active phase for biodiesel production under heterogeneous catalysis. *J. Catal*. 2013;300:30–36. http://dx.doi.org/10.1016/j.jcat.2012.12.016

14. Зотов Ю.Л., Заправдина Д.М. *Способ получения пластификатора для поливинилхлоридной композиции*: пат. 2643996 РФ. Заявка №2017100414, заявл. 09.01.2017; опубл. 06.02.2018, Бюл. № 4. 6 с.

About the authors:

Yuriy L. Zotov, Dr. Sci. (Chem.), Professor, Department of Organic and Petrochemical Synthesis Technology, Volgograd State Technical University (28, pr. im. V.I. Lenina, Volgograd, 400005, Russia). E-mail: ylzotov@mail.ru. Scopus Author ID 7003371961, RSCI SPIN-code 7543-9740, http://orcid.org/0000-0001-6301-0570

Daria M. Zapravdina, Assistant, Department of Organic and Petrochemical Synthesis Technology, Volgograd State Technical University (28, pr. im. V.I. Lenina, Volgograd, 400005, Russia). E-mail: zapravdinadasha94@gmail.com. RSCI SPIN-code 2913-1891, https://orcid.org/0000-0002-8654-2382

Evgeniy V. Shishkin, Dr. Sci. (Chem.), Professor, Department of Organic and Petrochemical Synthesis Technology, Volgograd State Technical University (28, pr. im. V.I. Lenina, Volgograd, 400005, Russia). E-mail: shishkin@vstu.ru. Scopus Author ID 7004314557, RSCI SPIN-code 3280-1800, https://orcid.org/0000-0002-2994-422X

Yuriy V. Popov, Dr. Sci. (Chem.), Professor, Department of Organic and Petrochemical Synthesis Technology, Volgograd State Technical University (28, pr. im. V.I. Lenina, Volgograd, 400005, Russia). E-mail: iury.popov@yandex.ru. Scopus Author ID 26028090100, RSCI SPIN-code 4582-3342, http://orcid.org/0000-0001-5659-028X

Об авторах:

Зотов Юрий Львович, д.х.н., профессор кафедры технологии органического и нефтехимического синтеза ФГБОУ ВО «Волгоградский государственный технический университет» (400005, Россия, Волгоград, пр-т им. В.И. Ленина, д. 28). E-mail: ylzotov@mail.ru. Scopus Author ID 7003371961, SPIN-код РИНЦ 7543-9740, http://orcid.org/0000-0001-6301-0570

Заправдина Дарья Михайловна, ассистент кафедры технологии органического и нефтехимического синтеза ФГБОУ ВО «Волгоградский государственный технический университет» (400005, Россия, Волгоград, пр-т им. В.И. Ленина, д. 28). E-mail: zapravdinadasha94@gmail.com. SPIN-код РИНЦ 2913-1891, https://orcid.org/0000-0002-8654-2382

Шишкин Евгений Вениаминович, д.х.н., профессор кафедры технологии органического и нефтехимического синтеза ФГБОУ ВО «Волгоградский государственный технический университет» (400005, Россия, Волгоград, пр-т им. В.И. Ленина, д. 28). E-mail: shishkin@vstu.ru. Scopus Author ID 7004314557, SPIN-код РИНЦ 3280-1800, https://orcid.org/0000-0002-2994-422X

Попов Юрий Васильевич, д.х.н., профессор кафедры технологии органического и нефтехимического синтеза ФГБОУ ВО «Волгоградский государственный технический университет» (400005, Россия, Волгоград, пр-т им. В.И. Ленина, д. 28). E-mail: iury.popov@yandex.ru. Scopus Author ID 26028090100, SPIN-код РИНЦ 4582-3342, http://orcid.org/0000-0001-5659-028X

The article was submitted: May 23, 2022; approved after reviewing: June 08, 2022; accepted for publication: July 15, 2022.

Translated from Russian into English by N. Isaeva
Edited for English language and spelling by Thomas Beavitt