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SCIENTIFIC PAPER

A NEW ECOLOGICALLY FRIENDLY PROCESS FOR THE SYNTHESIS OF SELECTIVE FLOTATION REAGENTS*

A new ecologically friendly synthesis of N-alkyl-O-ethylthiocarbamates from ethyl dixanthogenates, waste material from the xanthate production plant, and monoalkylamines has been performed in this work. Structure determination of the synthesized compounds and also corresponding intermediates has been performed by IR, ^{1}H-NMR and MS spectrometric methods. Residual dixanthogenates and thioncarbamates in waste water have been done by the gas chromatographic method and corresponding standard curve. It was confirmed that the reaction product was not present in water, while the concentration of dixanthogenates has been determined to be under the maximum contamination limit.

Key words: thioncarbamate; xantogenate; GC spectroscopy; ethyl dixanthogenate.

The production of thioncarbamates, broadly used flotation collectors [1-3], has been developed and they have been produced in large quantities in the past and present at the production plant of the chemical industry "Župa", Kruševac, Serbia. The production of either new or known collectors by the new method from the different starting material was and remains the development strategy of the company. In the past, large quantities of waste material from the xanthate production plant have been collected. It mainly consists of dixanthogenate, an oxidized xanthate by-product. New technologies for chemical transformation of those waste materials to a commercial product have been developed and protected according to the intellectual property right [4]. The optimal synthetic method has been developed at the laboratory and semi-industrial level. This new environmentally friendly technologies based on the waste material represent a significant contribution to the protection of the human environment. The extraordinary economic benefit has been attained by applying the innovative synthetic method at the semi-industrial level. The production of N-alkyl-O--ethyl thiocarbamate at the semi-industrial level, based on the innovative method, also generates a large quantity of waste water from the processes of raw material and product purification. Possible water contaminants are dixanthogenate, thiocarbamate product and oxidizer. Their concentration in the waste water should be under maximum contaminant concentration; otherwise, a necessary water purification process should be applied. Highly sensitive and reproductive analytical methods for their determination are used for running control tests of the water contaminants. In this way an enormous economic and environment protection benefit of the innovative process should be validated through the determination of the residual material concentration in waste water from a production plant.

Thioncarbamates are derivates of thiocarbamic acid (**1**):

$$H{-}N\overset{\displaystyle H}{\underset{\displaystyle H}{}}{-}\overset{\displaystyle S}{\overset{\|}{C}}{-}OH \qquad (\mathbf{1})$$

and represent the O-esters of thiocarbamic acid, and dialkyl thioncarbamates represent O-alkyl esters of N-alkyl thiocarbamic acid (**2**):

$$R_1 \diagdown \underset{H}{\overset{}{N}} - \underset{}{\overset{S}{\overset{\|}{C}}} - OR_2 \qquad (2)$$

These compounds are applied in flotation of copper and zinc ores as selective collectors [1]. They are also applied as oil additive [5], fungicides [6], bactericides [7], herbicides [8], pesticides [9] and as pharmaceutically active compounds [10]. Besides other procedures known in literature [7-11], *N*-alkyl-*O*-thioncarbamates can be obtained by the reaction of sodium- or potassium xanthogenates in an aqueous solution with primary or secondary aliphatic amines and elementary sulphur [12]. Thioncarbamates can also be obtained by the reaction of xanthogenates and amines in the presence of nickel(II) sulfate as catalyst [13]. Also, a kinetic and reaction mechanism between sodium ethyl xanthogen acetate and alkyl amines has been extensively investigated [14].

EXPERIMENTAL

The general method for purification of the waste oxidized product from xanthate production to ethyl dixanthogenate at the laboratory and semi-industrial level

The purification of the waste oxidized product from xanthate production, to obtain ethyl dixanthogenate, has been achieved by two successive dissolutions in hot water and filtration, in that way obtaining a 99% pure product (yield 55 %). The purity of ethyl dixanthogenate was checked by elemental analysis and the structure was confirmed by FTIR, ^{1}H- and ^{13}C-NMR spectroscopic techniques.

The general method for the synthesis of *N*-alkyl-*O*--ethylthioncarbamate at the laboratory level

In a three-necked flask, equipped with a magnetic stirrer, a dropping funnel, a condenser and a thermometer, 100 cm^3 of water and 20.65 g (0.075 mol) of 98% diethyl dixanthogenate were added. A solution of 12.25 cm^3 (0.15 mol) of 68% ethyl amine was being added for one hour with a vigorous stirring. In that way, the increase of temperature to 30 °C occurred. After that period, 20.50 g (0.075 mol) of sodium hypochlorite (130 g of active chlorine/1000 cm^3) was added dropwise. The temperature of the reaction mixture gradually rose to 45 °C within one hour and a half, after that time the reaction was completed. Sulphur particles precipitated in the quantity almost corresponding stoichiometrically to the reaction yield.

The reaction mixture was filtered on the Buchner funnel, the precipitated sulphur was separated as the filtration cake from an aqueous emulsion phase of *N*-ethyl-*O*-ethylthioncarbamate. The product was isolated from the filtrate by two ethereal extractions, dried with sodium-sulphate and ether was distilled at atmospheric pressure. A pure product was obtained by fractional vacuum distillation at 105 °C/(2200 Pa). 21.50 g of *N*-ethyl-*O*-ethylthioncarbamate is obtained, representing the yield of 93.5%. The GC purity was 97.7%. All other *N*-alkyl-*O*-ethyl thioncarbamates were synthesized in an analogous manner to the above procedure, using the appropriate amines under the reaction conditions presented in Table 1. Analytical data of the synthesized compounds (boiling point; GC purity): *N*-propyl-*O*-ethylthioncarbamate (126-8 °C/2200 Pa; 96.4%), *N*-isopropyl-*O*-ethylthioncarbamate (127-129 °C/2200 Pa; 95.8%) and *N*-butyl-*O*-ethylthioncarbamate (130-132 °C/2200 Pa; 98.2%).

Experimental procedures for the isolation of intermediates and products of the reaction

In a 250 cm^3 three-necked flask equipped with a magnetic mixer, a dropping funnel, a condenser and a thermometer, 100 cm^3 of water and 18.52 g (0.075 mol) of 98% diethyl dixanthogenate were added. Thereafter, by a gentle stirring a 12.25 cm^3 (0.15 mol) of 68% ethyl amine was being added for half an hour. The temperature rose to 30 °C. The reaction mixture was filtered, the filtration cake consisted mainly of sulphur (2.0 g, determined analytically precipitating as sulfate). The filtrate was then transferred to the separation funnel, the organic phase separated in the upper layer (*N*-ethyl-*O*-ethyl thionocarbamate, confirmed by FTIR, ^{1}H-NMR, GC MS/MS spectroscopic data, 5 g of crude product). The aqueous solution was transferred into a beaker and hydrochloric acid (1:1) was added with a continuous stirring until pH of the solution became slightly acidic (pH ≈6). At the bottom of the beaker a light yellow substance, insoluble in water, ethyl xanthogenic acid was deposited. Diethyl ether extract of ethyl xanthogenic acid was dried with sodium sulfate. Ether was distilled, and the purity of ethyl xanthogenic acid (7.0 g) was determined potentiometrically. The structure of ethyl xanthogenic acid was confirmed by FTIR, ^{1}H- and ^{13}C-NMR and GC MS/MS data (Table 3).

In the second experiment, repeated as the above described, the isolated amine salt of ethyl xanthogenic acid (the lower aqueous solution) was filtered to remove sulphur, and then treated with 20.00 g (0.075 mol) of sodium hypochlorite (150 g of active chlorine in 1000 cm^3). In the course of time the temperature was maintained at 45 °C, for 1 h. After the reaction was completed the reaction mixture was filtered. The filtration cake contained diethyl dixanthogenate having a

melting point 30-31 °C (lit. m.p., 32 °C [15]), (the structure confirmed by FTIR, ^{1}H- and ^{13}C-NMR, GC MS/MS data, Table 3).

In the third experiment, the aqueous phase which contains amine salt of ethyl xanthogenic acid, was treated with zinc(II) sulphate precipitating salt of ethyl xanthogenic acid. Zinc(II) diethylxanthogenate was characterized by FTIR, ^{1}H- and ^{13}C-NMR techniques (Table 3) as well as the zinc content which was determined by the atomic absorption spectroscopy. In that way it was undoubtedly proved that the ammonium salt of ethyl xanthogenic acid was an intermediary product presented in a reaction mechanism by Scheme 1.

The general method for the synthesis of *N*-alkyl-*O*-ethylthioncarbamate at the semi-industrial level

The established optimal laboratory synthesis of *N*-alkyl-*O*-ethylthioncarbamates was, in the next step of the technology transfer, applied at the semi-industrial level. The purification of the waste oxidized product from xanthate production to ethyl dixanthogenate was achieved in the same way as described for the laboratory purification process, starting from 1 t of the waste material, in that way obtaining 550 kg (equally to the yield obtained at the laboratory level). The analogous synthetic method of the synthesis of *N*-alkyl-*O*-ethylthioncarbamates, to that at the laboratory level, was applied at the semi-industrial level, and the quantities of the reactants were adjusted for the synthesis of 215 kg of pure *N*-alkyl-*O*-ethylthioncarbamates. The additional optimization of the semi-industrial synthetic process was performed to attain the yields of *N*-alkyl-*O*-ethylthioncarbamates obtained at the laboratory level. The confirmation of the structure and the purity of the obtained products at the semi-industrial level have proved the applicability of the new ecological synthetic method having, besides the environmentally friendly impact, an extraordinary economic benefit of such a production.

Instrumental techniques used for structure determination of synthesized compounds

The ^{1}H-NMR spectral measurements were performed on a Bruker AC 250 spectrometer at 62.896 MHz. The spectra were recorded at room temperature in deuterated chloroform (CDCl_3) in 5 mm tubes. The chemical shifts are expressed in ppm (δ) values referenced to the TMS (tetramethylsilane) reference standard signal.

All mass spectra were recorded on a Thermo-Finnigan Polaris Q ion trap mass spectrometer, including TraceGC 2000 (ThermoFinnigan Corp., Austin, TX, USA), integrated GC-MS/MS system.

Fourier-transform infrared (FTIR) spectra were recorded in a transmission mode using a BOMEM (Hartmann & Braun) spectrometer.

Analytical methods for determination of residual ethyl dixanthogenate in waste water

The first analytical method is based on the determination of carbon-disulfide released from the sample containing residual dixanthogenate in waste water and its absorption at Wiles' reagent. The concentration of the residual dixanthogenate was determined by a colorimetric method using UV spectrophotometer.

The second analytical method is based on the extraction of residual dixanthogenates and thioncarbamates in waste water using GC method for their quantification.

Determination of ethyl dixanthogenates in waste water by UV method

In a reaction flask (4) (Figure 1), connected with the apparatus for absorption of released carbon disulfide, standard solutions of ethyl dixanthogenates were added.
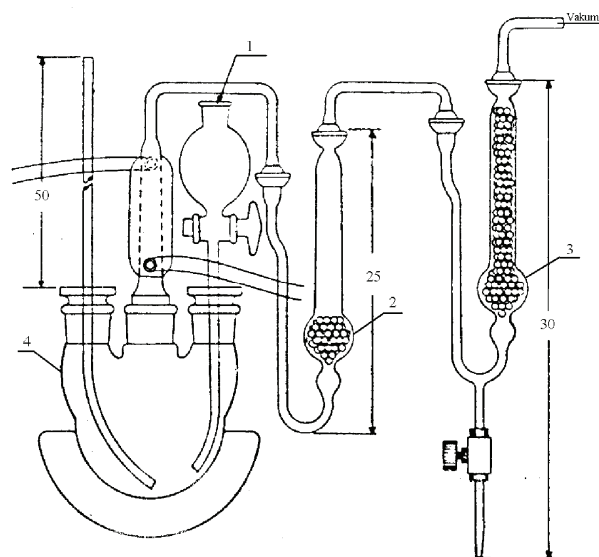

Figure 1. Apparatus for determination of residual dixanthogenate and thioncarbamates in waste water.

Standard solutions of ethyl dixanthogenates (1, 2, 3, 5 and 8 cm³) were prepared in the following manner: 0.04 g of the substance was dissolved in 100 cm³ of chloroform and 5 cm³ of the obtained solution diluted to 100 cm³ with chloroform. In the first adsorption column (2) 200 cm³ of distilled water was added and 10 cm³ of the lead acetate solution, while in the second column (3) 12.5 cm³ of Wiles' reagent was added (0.05 g copper acetate dissolved in 25 cm³ distilled water, 975 cm³ of ethanol, 1 cm³ of diethylamine and 20 cm³ of tri-

ethanolamine). The apparatus was assembled and the reaction bottle was slowly heated at atmospheric pressure. When the temperature reached 90 °C vacuum was carefully turned on and from the dropping funnel (1), 40 cm^3 (5 moldm^{-3}) of sulphuric acid was added. The reaction mixture was left for 30-45 min to complete the reaction, the apparatus was disassembled and Wiles' reagent was drained into a common container of 25 cm^3. The column was washed three times with 3-4 cm^3 of ethanol (95%), the volume of the ethanol was adjusted till the mark and agitated. The absorption of the solution was measured at 380 nm using a 1 cm cuvette. The reference solution was prepared by diluting with 12.5 cm^3 of Wiles' reagent with ethanol untill 25 cm^3. The standard curve was obtained by ratio of the absorption values for the given concentrations of ethyl dixanthogenates. UV-analyses were performed at UV/Vis spectrophotometer Perkin-Elmer, Lambda 15.

The analysis of the waste water sample was performed by an analogous method as described for the standard curve preparation. A sample of waste water was introduced into the reaction flask (Figure 1), an excess of 200 cm^3 of distilled water was added following the above described procedure. The concentration of residual ethyl dixanthogenates was calculated from the values of UV absorption measurements using the following standard curve: A = (0.02±0.001) + (0.32± ± 0.02)c, r = 0.995; sd = 0.04; n = 6, where r is the correlation coefficient, sd the standard deviation and n the number of data included in the correlation.

A gas chromatographic (GC) method for the determination of residual *N*-alkyl-*O*-ethyl thioncarbamate

A sample of the waste water (500 cm^3) after the synthesis was transferred into the separation funnel, and extracted with 300 cm^3 of isobutyl alcohol. After the phase separation, the organic layer was analyzed by injection of 0.1 μl of sample into GC chromatograph. GC analysis was performed on Perkin-Elmer gas chromatograph series 8700, equipped with the flame ionization detector and columns filled with: 10% of SP--2410 at Supelcort (100/120) and 5% of OV-210 at

Chromosorb WH/P (80/100). An internal standard method was used for quantification of residual dialkyl thioncarbamates in the waste water.

Chromatographic conditions:
-   injector temperature 250 °C;
-   detector temperature 270 °C;
-   column temperature-program mode: Supelcort column 50 °C → 5 °C/min → 150 °C; Chromosorb - WH/P column 50 °C → 5 °C/min → 130 °C;
-   carrier gas: nitrogen (99.99 %);
-   nitrogen flow: 25 cm^3/min;
-   air flow: 250 cm^3/ min (99.99 %);
-   hydrogen flow: 25 cm^3/ min (99.99 %);
-   column: inner diameter 2 mm, length 30 m.

RESULTS AND DISCUSSION

The synthesis of *N*-alkyl-*O*-ethylthioncarbamates starting from ethyl dixanthogenate and alkylamines was performed according to the above described experimental procedure, and experimental parameters for the synthesis are given in Table 1.

Based on the results given in Table 1, it could be observed that high yields and satisfactory purity of synthesized *N*-alkyl-*O*-ethylthioncarbamates were achieved starting from waste ethyl dixanthogenate. The structure of synthesized *N*-alkyl-*O*-ehtylthioncarbamates is confirmed by IR, ^{1}H-NMR and MS spectrometric data (Table 2).

The assumed mechanism of this reaction was confirmed by isolation and structure determination of the reaction intermediates and products (Table 3). Namely, the intermediate in the first step of the heterolysis reaction of dixanthogenate S-S bond is amine salt of ethyl xanthogenic acid which was isolated. The presence of the sulphur as a product of decomposition of sulphenamide in the reaction mixture after the filtration was nearly equal to stehiometrically calculated to the yield according to the presented reaction mechanism.

In the third step, an oxidation of amine salt of ethyl xanthogenic acid by the use of sodium hypochlorite, a mixed dialkyl dixanthogenate wass also isolated as a crucial evidence of the reaction mechanism. Ba-

Table 1. Yield and purity of the synthesized N*-alkyl-*O*-ethylthioncarbamates*

Compound	Reaction time, h	Temperature, °C	Yield		Overall yield[a]	GC
			g	%	%	%
EtOC(S)NHEt	2.4	30-35	21.50	93.5	52.3	97.7
EtOC(S)NHnPr	2.9	30-35	23.40	93.4	51.4	96.4
EtOC(S)NHiPr	3.1	30-45	22.40	86.0	47.3	95.8
EtOC(S)NHBu	3.6	30-40	25.36	94.8	51.2	98.2

[a]Calculated on the basis of starting ethyl dixanthogenate

Table 2. FTIR, ^{1}H-NMR and CI MS data of synthesized N-alkyl-O-ethylthioncarbamates

Thioncarbamate	IR, v_{max} / cm^{-1}	^{1}H-NMR, δ / ppm	MS, *m/z*
EtOC(S)NHEt	3264, 2978, 2935, 1524, 1450, 1405, 1331, 1298, 1205, 1102, 1055, 1028, 944, 868, 800, 772	0.95-1.40 (6H, *m*[a], N-CH$_2$-CH$_3$, O-CH$_2$-CH$_3$), 3.10-3.75 (2H, *dq*[a], N-CH$_2$), 4.40 (2H, *m*, O-CH$_2$), 6.20-6.65 (1H, *bs*[a], NH)	133
EtOC(S)NH(nPr)	3260, 2965, 2934, 2876, 1542, 1458, 1405, 1380, 1353, 1332, 1297, 1260, 1198, 1142, 1117, 1075, 1041, 1015, 888, 773	0,96 (3H, *t*[a], (CH$_2$)$_2$-CH$_3$), 1,15-1,90 (5H, *m*, O-CH$_2$CH$_3$, CH$_2$CH$_2$CH$_3$), 3.10-3.55 (2H, *m*, N-CH$_2$), 4.48 (2H, *m*, OCH$_2$), 6.64-7.10 (1H, *bs*, NH)	147
EtOC(S)NH(iPr)	3252, 2977, 2933, 2875, 1519, 1457, 1400, 1367, 1333, 1312, 1210, 1108, 1042, 993, 904, 834, 772, 714, 653	1.10-1.40 (9H, *m*, NCH(CH$_3$)$_2$, OCH$_2$CH$_3$), 3.95 (1H, *m*, NCH), 4.42 (2H, *m*, OCH$_2$), 6.10-6.55 (1H, *bs*, NH)	147
EtOC(S)NHBu	3264, 2962, 2930, 2878, 1546, 1454, 1396, 1384, 1350, 1336, 1295, 1264, 1188, 1132, 1110, 1065, 1031, 1007, 879, 765	0.95-1.40 (3H, *t*, CH$_2$CH$_3$), 1.26-1.34 (3H, *t*, O-CH$_2$CH$_3$), 1.44-1.56 (2H, *sq*[a], CH$_2$CH$_3$), 2.81-2.92 (2H, *t*, NCH$_2$-), 3.50-3.62 (2H, *q*[a], OCH$_2$CH$_3$), 6.50-7.04 (1, bs, N-H)	161

[a] *m* - multiplet; *dq* - double quartet; *bs* - broad singlet; *t* - triplet; *sq* - sextet; *q* - quartet

Table 3. FTIR, ^{1}H-NMR and MS data of the reaction intermediates and products

Compound	IR, v_{max} / cm^{-1}	^{1}H-NMR, δ / ppm	MS, *m/z*
[EtOC(S)S]$_2$	2976, 2932, 2870, 1450, 1448, 1370, 1350, 1276, 1145, 1082, 1025, 1015, 890, 786	1.32 (6H, *t*, OCH$_2$CH$_3$), 3.64 (2H, *q*, OCH$_2$CH$_3$)	242.41
EtOC(S)SH	3445, 2986, 2926, 2493, 1730, 1718 1644, 1543, 1460, 1422, 1320, 1248, 1118, 814, 744, 670, 534	1.10 (3H, *t*, OCH$_2$CH$_3$), 1.54 (2H, *bs*, SH), 3.60 (2H, *q*, OCH$_2$CH$_3$)	122.21
(EtOC(S)S)$_2$Zn	2982, 2934, 2870, 1454, 1342, 1255, 1131, 1061, 1040, 892	1.28 (9H, *t*, OCH$_2$CH$_3$), 5.14 (2H, *m*, OCH$_2$CH$_3$)	-

sed on the identification of the isolated compounds, the assumed mechanism of the reaction was proved in that way.

In that way, the optimal reaction condition for the synthesis of *N*-alkyl-*O*-ethyl thioncarbamate at the laboratory and semi-industrial level was established.

The investigated synthesis presents a nucleophilic heterolysis of the S-S bond of dixanthogenate (I) using amine (II) producing sulphenamide (III) and amine salt of alkyl xanthogenic acid (IV) (Scheme 1, reaction (3)). In the next consecutive step (reaction (4)), sul-

phenamide (III) is decomposed into sulphur and alkyl thioncarbamate (V). Further on, the oxidation of amine salt (IV) is performed by using sodium hypochlorite (VI) producing alkyl dixanthogenate (I) (reaction (5)) and all reaction steps are successively repeated, *i.e.*, the present amine performs heterolysis of S-S bond of the obtained alkyl dixanthogenate [4].

The analysis of the waste water after the production of *N*-alkyl-*O*-ethylthioncarbamate according to the described procedure for the determination of residual
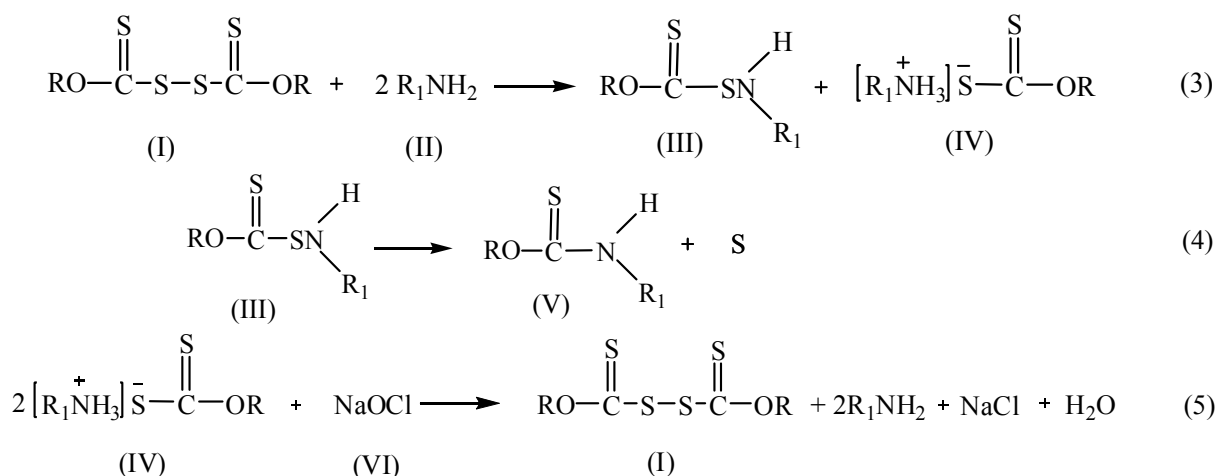

Scheme 1. The established reaction mechanism of the synthesis of N-alkyl-O-ethyl thioncarbamate from ethyl dixanthogenate.

Table 4. Concentrations of ethyl dixanthogenate in waste water

Compound	Sample quantity (cm^3)	Concentration of ethyl dixanthogenate	
		$c \times 10^3$ / mmol dm^{-3}	$c \times 10^2$ / mg dm^{-3}
EtOC(S)NHEt	70.0	21.36	58.00
EtOC(S)NHnPr	85.0	20.09	53.80
EtOC(S)NHiPr	85.0	19.98	54.31
EtOC(S)NHBu	80.0	18.45	50.29

ethyl dixanthogenate and using obtained calibration curve gave their residual concentrations in waste water presented in Table 4.

Based on the results shown in Table 2, the minimal concentration of residual ethyl dixantogenate is detected in the waste water from the synthesis of *N*-butyl--*O*-ethylthioncarbamate, while the maximal concentration from the synthesis of *N*-ethyl-*O*-ethylthioncarbamate. A sample of the waste water, after the synthesis, should contain from 20 to 160 μg/dm^3 of the residual ethyl dixanthogenate. From that point of view all concentrations in the investigated water are below the maximal concentration in the waste water.

The analysis of the waste water using GC method showed that there were no alkyl thioncarbamate in the waste water. The obtained GC chromatogram of the treated sample of the waste water from the synthesis of *N*-alkyl-*O*-ethylthioncarbamate indicates no presence of residual *N*-alkyl-*O*-ethylthioncarbamates in the waste water. Only the presence of the extraction medium (isobutyl alcohol) was recorded.

CONCLUSION

This work describes the optimal synthesis of *N*-alkyl-*O*-ethylthioncarbamates from ethyldixanthogenates which were isolated from the waste material from the xanthate production plant. The synthetic method was developed at the laboratory and semi-industrial level. A high level of conversion of starting materials into the products was achieved (86 to 94.8%). In addition, the analysis of the waste water from semi-industrial synthesis was performed and the obtained results showed that ethyldixanthogenates can successfully be determined. Ethyldixanthogenates were present in the waste water in quantities of around 18.45×10^{-3} mmol dm^{-3}, while *N*-alkyl-*O*-ethylthioncarbamates were not detected.

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