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DENITRATION OF WASTEWATER GENERATED BY NITROSATION OF ORGANIC COMPOUNDS

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Abstract: Subject of the article was to study the method aimed at denitration of liquid wastes that appear during the nitrosation of organic compounds. Liquid waste represents an aqueous solution of sodium sulfate with sodium nitrate and nitrite as admixtures. The method involves addition of sulfuric acid to the wastes followed by drying and thermal treatment of a salt mixture at temperature above 150 °C. Experimental study revealed that sodium nitrite fully decomposes in the solution during the drying resulting in formation of sodium sulfate, nitrogen oxide, and nitrogen dioxide. Solid-phase interaction of sodium hydrogen sulfate and sodium nitrate was investigated by combined DSC-TG technique in the temperature range 100 - 270 °C. The mixture of salts was obtained by drying the aqueous solution. It was shown that the reaction rate is defined by the removal rate of vapors formed nitric acid.

Keywords: *sodium sulfate, sodium nitrate, sodium hydrogen sulfate, recycling, thermal analysis, polymorphic transitions*

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INTRODUCTION

Modern production of N-dialkylnitrosamines, general formula R_1R_2NNO, where R_1, R_2 - alkyl radicals, is based on nitrosation of dialkylamines by sodium nitrite in the presence of sulfuric acid [1 – 2]. Nitrosodialkylamines are then recovered from the reaction mixture by rectification as a distillate mixed with water. Distillation residue is an aqueous solution of sodium sulfate, nitrate, and nitrite in a total concentration about 30 wt. %, it also contains nitrosodialkylamines up to several percents. The main problem of disposing of this solution is the content of highly toxic nitrosamines.

Currently, at some companies, this solution is dried, forming Na_2SO_4 with a high content (up to 25 wt. %) of $NaNO_3$ and $NaNO_2$. Reduction of the content of residual $NaNO_3$ is achieved by fractional crystallization of Na_2SO_4. Thanks to a greater solubility of $NaNO_3$ in water compared with solubility of Na_2SO_4, it is possible to reduce the residual content of $NaNO_3$ in Na_2SO_4 up to 6 - 10 wt. %. A mother-water formed is enriched with nitrites, nitrates, and nitrosamines. However, the method cannot solve the waste problem completely; it allows only partial reduction of the amount of new waste. Mother-water, being highly toxic waste, requires further processing; dry Na_2SO_4, with a high residual content of $NaNO_3$ is also heavily polluted by nitrosamines.

Well-known methods of acid decomposition of salts can be the basis for the development of recycling technology of this solution. There is a patented processing method [3] for sodium sulfate and carbonate containing solution, wherein sulfuric acid is added to the solution; afterwards the resultant mixture is dried. Carbonate-ion in acidic media decomposes when exposed to heating generating carbon dioxide and water. The advantage of this method is a combination of two processes: decomposition of the carbonate and production of dry Na_2SO_4 from the solution.

We have previously proposed and patented [4] a method for disposal of sulfate-nitrate solution. Sulfuric acid and urea are added to the solution, then the resultant mixture is dried and held at temperature about 150 - 200 °C, to trigger the interaction between $NaNO_3$ with urea in acidic media forming carbon dioxide, ammonia and water. Thus, this method allows obtaining substantially purified Na_2SO_4. One can expect that disposing the solution with only sulfuric acid can be an efficient method: mixture obtained in the same way is to be dried and then held at high temperature to initiate decomposition of $NaNO_2$ [5, 6] according to the scheme:

$$2NaNO_2 + H_2SO_4 \rightarrow Na_2SO_4 + NO_2\uparrow + NO\uparrow + H_2O \quad (1)$$

Sulfuric acid in excess reacts with Na_2SO_4 producing $NaHSO_4$. Then one can expect that a reaction similar to the sulfuric acid decomposition of calcium difluoride or sodium chloride [7 – 9] will proceed:

$$NaHSO_4 + NaNO_3 \rightarrow Na_2SO_4 + HNO_3\uparrow \quad (2)$$

In general, reactions in a solid mixture are slow; however phase transitions can substantially accelerate the reaction. Specifically, Na_2SO_4 has two polymorphic transitions [10] at 180 °C and 240 °C which can accelerate reaction (2). Nevertheless it should be taken into account that there is the competing decomposition path (3) for $NaHSO_4$ at elevated temperatures which may lead to decaying reaction (2).

$$2NaHSO_4 \rightarrow Na_2S_2O_7 + H_2O\uparrow \quad (3)$$

Partial decomposition of nitric acid in the vapor phase [11, 12] occurs at high temperature which generates nitrogen oxide, nitrogen dioxide and oxygen:

$$2HNO_3 \rightarrow H_2O + 2NO_2 + 0{,}5O_2 \quad (4)$$

$$2NO_2 \rightarrow 2NO + O_2 \quad (5)$$

This paper represents the results of investigation of solid-phase interaction of $NaNO_3$ with $NaHSO_4$ in the presence of Na_2SO_4. This solid mixture was obtained by co-crystallization from the aqueous solution. The combined differential scanning calorimetry (DSC) and thermogravimetry (TG) technique was applied for experimental study. Heat effects of the stages have been estimated and the composition of the gaseous reaction products has been determined. The results obtained are the basis for the design of the recycling technology of wastewater which appears in the course of organic compounds nitrosation.

MATERIALS AND METHODS

The solutions of salts used for experimental study had the composition similar to the industrial ones. The following reagents were used: Na_2SO_4 (99.5 wt. %, according to GOST 4166 - 76), $NaNO_3$ (99.8 wt. %, according to GOST 4168 - 79), $NaNO_2$ (99.0 wt. %, according to GOST 4197 - 74), H_2SO_4 (93.6 - 95.6 wt. %, according to GOST 4204 - 77).

The salt solution was prepared in polyethylene vessel equipped with water bath and stirrer. Weighed quantities of dry salts were dissolved in distilled water; the vessel was heated to 45 - 60 °C in order to complete dissolution. After that the calculated quantity of sulfuric acid was dosed so as to avoid abrupt fluid overheating. Then reaction mass was being mixed at 45 - 60 °C during 1 hour. Content of $NaNO_2$ in the reaction mass was measured by the permanganometry [13], content of $NaHSO_4$ - by potentiometric titration [14] by Starorius PB-11 potentiometer, content of $NaNO_3$ - by colorimetric method [15, 16] using Shimadzu UVmini-1240 UV-spectrophotometer. Finally the reaction mass was evaporated at 90 - 110 °C until constant weight. Dry mixture of salts was analyzed for a content of $NaNO_2$, $NaHSO_4$, and $NaNO_3$ using the methods mentioned above.

Thermoanalytical experiments were performed by using Setaram Sensys Evo TG-DSC instrument in open pans under air at heating rate 3 $°C \cdot min^{-1}$. Data processing was implemented by the TDPro [17] program developed by ChemInform Saint Petersburg Ltd.

The composition of gaseous reaction products was studied in a reactor comprising nickel tube (inner diameter - 36 mm, length - 470 mm) with outer resistive heater. The temperature was measured by a cased thermocouple placed in the inner volume of the reactor. The experiment was carried out as follows: the dry salt mixture in amount of 5 - 20 g was loaded in a glass cell, which was placed in the reactor, and was heated to the desired temperature. An inert gas flow was used for effective evacuation of the gaseous reaction products. Three glass traps (Richter absorbers) were successively placed on the outlet of the reactor. The traps were filled with wash-water: the first and the second - with 20 wt. % solution of NaOH, and the last one was filled with solution containing 15 wt. % H_2O_2 and 10 wt. % HNO_3. The experiment was stopped after discoloration of exhaust gas. The bulk solid was unloaded from the cell, weighed and analyzed. Content of $NaHSO_4$ and $NaNO_3$ was measured using the methods mentioned above. Connection pipes between the reactor and the traps were washed with distilled

water for removal of traces of nitric acid retained on the inner surface. The water was analyzed for the content of nitric acid using UV-spectrophotometery. NaOH solution from the traps was analyzed for the content of $NaNO_2$ and $NaNO_3$. The solution from the last trap was analyzed for the content of nitric acid for determining quantity of NO.

RESULTS AND DISCUSSION

The dry salt mixture was obtained from water solution of the following composition: Na_2SO_4 - 24 wt. %, $NaNO_3$ - 6 wt. %, $NaNO_2$ - 1.8 wt. %. Sulfuric acid (94.5 wt. %) was added into the solution in the amount of 1 mole of the acid per 2 moles of nitrate- and nitrite-ion, contained in the solution. Then, reaction mass was analyzed and a conversion of $NaNO_2$ was calculated. Table 1 shows that the heating of the solution up to 60 ºC practically decomposes nitrite. Fourth run, which was performed with a flow of nitrogen over a surface of the solution, showed, that an effective removal of decomposition products (NO_x) can significantly increase depth of nitrite decomposition, which reaches 97.8 %.

Table 1. *The decomposition of $NaNO_2$ in the salt-containing solutions acidified by sulfuric acid*

Max. temperature [ºC]	Average heat rate [ºC·min^{-1}]	Treatment time[(a)] [min]	Sodium nitrite conversion [%]
46	0.60	20.5	84.0
51	0.65	13.0	85.2
57	0.54	0.0	85.0
60	0.90	12.0	97.8[(b)]

[(a)] treatment time at maximum temperature
[(b)] flow of nitrogen over a surface of the solution

Figure 1 shows the DTG and DSC curves of the sample of the salt mixture composition: Na_2SO_4 - 87.35 wt. %; $NaHSO_4$ - 7.15 wt. %; $NaNO_3$ - 5.30 wt. %; H_2O - 0.20 wt. %).

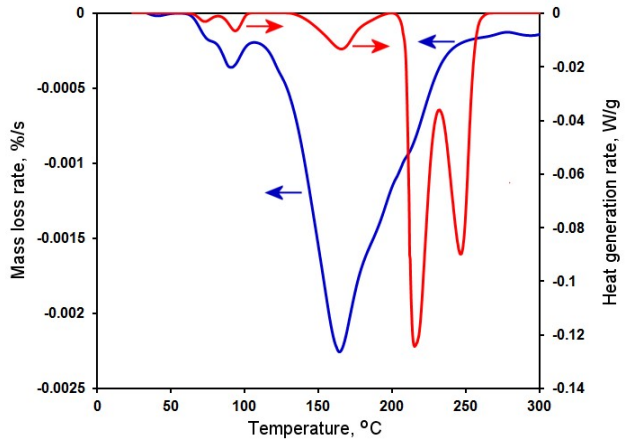

Figure 1. *DTG and DSC curves of the sample of the salt mixture, obtained from the solution by drying at 95 °C*

Two low-temperature overlapping peaks on the DSC curve can be associated with successive loss a water by hydrates $Na_2SO_4{\cdot}10H_2O$ and $Na_2SO_4{\cdot}7H_2O$ followed by

water evaporation [10]. Measured heat absorption - 4.6 $J \cdot g^{-1}$, recalculated per unit of mass of water - 2300 $kJ \cdot kg^{-1}$, which is in good accordance with the water evaporation heat at 80 °C [18] - 2308 $kJ \cdot kg^{-1}$.

Within the temperature range 100 - 250 °C the major peak is observed on the DTG curve which corresponds to reaction (2), i.e. release of gaseous nitric acid. According to the results obtained overall mass loss of the sample due to water and nitric acid evaporation is 3.28 %. Initial moisture of the sample is 0.2 %; therefore mass loss due to nitric acid evaporation is 3.08 %, which corresponds to 79.2 % conversion of sodium nitrate. The TG peak considered above corresponds to three heat absorption DSC peaks (the first is between 132 and 191 °C and two overlapping peaks are located between 195 and 266 °C). Considering that the first peak corresponds to reaction (2), its heat effect calculated in accordance with data [19] is 608 $J \cdot g^{-1}$. Recalculation of the heat effect per unit of mass of $NaNO_3$ in the sample gives the value 32.2 $J \cdot g^{-1}$; however, experimental value of the overall heat effect is 7.6 $J \cdot g^{-1}$. In means that conversion of $NaNO_3$ on this stage is 24 %.

Second and third DSC peaks cannot be separated, therefore the total heat absorption can be estimated as 70 $J \cdot g^{-1}$. As full conversion of $NaNO_3$ is 79.2 %, one can expected a heat absorption of 25.5 $J \cdot g^{-1}$. Taking into account partial decomposition of $NaNO_3$ on the first stage one can estimate heat absorption on the second stage as 17.9 $J \cdot g^{-1}$. Difference (52.1 $J \cdot g^{-1}$) between calculated and experimental value is caused by polymorphic transitions [10].

Special DSC experiment was performed to determine heat effects of the polymorphic transitions in pure Na_2SO_4. Figure 2 shows the DSC curve. Two separated peaks represent polymorphic transitions in Na_2SO_4 in the temperature range 215 - 250 °C. Heat effect of the first polymorphic transition ($\alpha \rightarrow \beta$) is 14 $J \cdot g^{-1}$ and heat effect of the second polymorphic transition ($\beta \rightarrow \gamma$) is 50 $J \cdot g^{-1}$. Total heat of the polymorphic transitions per unit of mass of Na_2SO_4 in the sample (87.35 wt. %) is 56 $J \cdot g^{-1}$, this confirms that second and third peaks on DSC curve (Figure 1) are correspond indeed to the polymorphic transitions in Na_2SO_4.

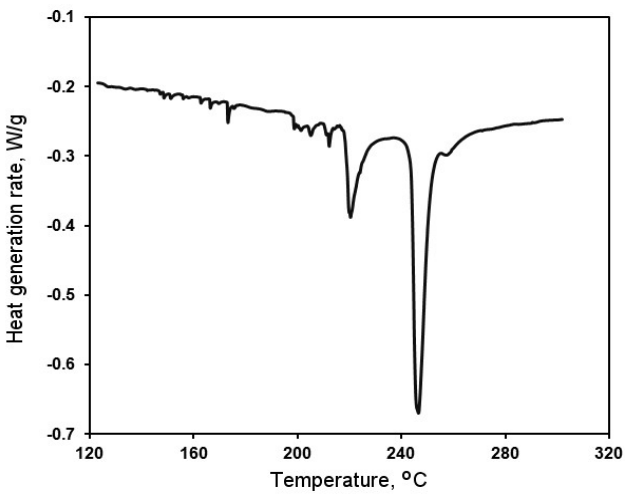

Figure 2. *DSC curve of pure Na_2SO_4*

The results of DSC-TG experiments show that $NaNO_3$ and $NaHSO_4$ react in two stages. One can guess that two different phases are formed when drying of the salt solution: the

phase, in which $NaNO_3$ and $NaHSO_4$ react within temperature range 150 - 200 °C and the phase, in which $NaNO_3$ and $NaHSO_4$ react during the two polymorphic transitions within temperature range 200 - 250 °C.

DSC analysis of salts obtained at different drying temperatures was performed for a more detailed study of this phenomenon. Figure 3 shows DSC curves of two samples with the following compositions: sample 1 (Na_2SO_4 - 87.04 wt. %, $NaHSO_4$ - 7.10 wt. %, $NaNO_3$ - 5.26 wt. %, H_2O - 0.60 wt. %), obtained at drying temperature 95 °C, sample 2 (Na_2SO_4 - 87.20 wt. %, $NaHSO_4$ - 7.12 wt. %, $NaNO_3$ - 5.28 wt. %, H_2O - 0.40 wt. %), obtained at drying temperature 120 °C.

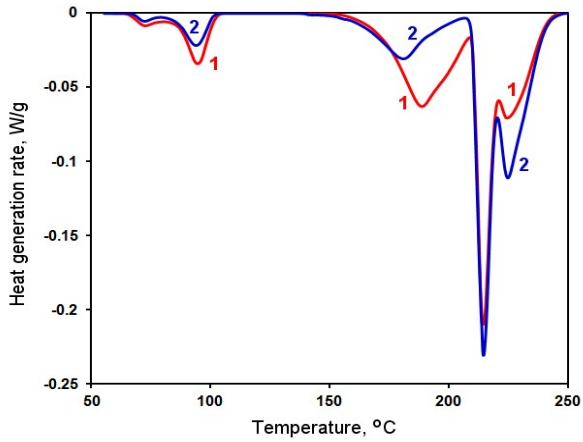

Figure 3. *DSC curves of two samples, obtained in different conditions*

Heat effects of the stages are presented in Table 2. Analysis of the DSC curves shows that evaporation of residue moisture and destruction of hydrates occur in two stages (peak 1). The second peak corresponds to reaction (2). Comparison of the heat effects reveals that the sample, obtained at higher temperature contains smaller amount of the first phase and reaction (2) proceeds mostly at temperatures over 210 °C, when polymorphic transitions in Na_2SO_4 occurs.

Table 2. *Heating values of the stages*

	Q1[(a)] [J·g^{-1}]	**Q2[(b)] [J·g^{-1}]**	**Q2[(c)] [J·g^{-1}]**
Sample 1	- 14.63	- 23.80	- 41.98
Sample 2	- 8.38	- 15.80	- 57.50

(a) Q1 – heating value of the peak 1 at temperature range 50 - 110 °C
(b) Q2 – heating value of the peak 2 at temperature range 145 - 208 °C
(c) Q3 – heating value of the peaks 2 and 4 at temperature range 208 - 260 °C

The composition of gaseous reaction products and the conversion of $NaNO_3$ were determined by using the reactor. The results of heat treatment of the salt mixture containing $NaNO_3$, $NaHSO_4$, and Na_2SO_4 are presented in Table 3.

Since the great majority of the nitric acid is captured by the first trap (concentration of the sodium nitrite and nitrate in the second trap is about ten times smaller than in the first one), one can assume that all the nitric acid is captured by the first trap.

Table 3. *Results of the heat treatment of the dry salt mixture containing sodium nitrate, sodium sulfate, and sodium hydrogen sulfate. Origin composition of the salt mixture: $NaNO_3$ - 5.26 wt. %, $NaHSO_4$ - 7.10 wt. %, Na_2SO_4 - 87.65 wt. %*

T[(b)] [°C]	τ[(c)] [min]	Final composition of the salt mixture		φ[(d)] [%]	m[(e)] [g]	Wash-water from the trap 1			η[(g)] [%]
		Comp.	C[(a)] [wt.%]			m[(f)] [g]	Comp.	C[(a)] [wt. %]	
190-200	40	$NaNO_3$ $NaHSO_4$ Na_2SO_4	2.09 3.38 94.53	61	0.12	16.904	$NaNO_3$ $NaNO_2$	0.46 0.14	18
210-220	40	$NaNO_3$ $NaHSO_4$ Na_2SO_4	2.04 3.49 94.47	63	0.11	20.054	$NaNO_3$ $NaNO_2$	0.41 0.07	10
210-220	45	$NaNO_3$ $NaHSO_4$ Na_2SO_4	1.90 2.10 96.00	65	0.06	23.011	$NaNO_3$ $NaNO_2$	0.12 0.06	17
210-220	50	$NaNO_3$ $NaHSO_4$ Na_2SO_4	1.50 2.67 95.83	72	0.09	23.366	$NaNO_3$ $NaNO_2$	0.19 0.08	13
210-225[(h)]	45	$NaNO_3$ $NaHSO_4$ Na_2SO_4	0.99 1.83 97.18	82	0.18	23.032	$NaNO_3$ $NaNO_2$	1.43 0.11	9
200-220[(i)]	8	$NaNO_3$ $NaHSO_4$ Na_2SO_4	0.70 1.50 97.80	87	0.03	23.098	$NaNO_3$ $NaNO_2$	1.56 0.09	8
220-230[(i)]	10	$NaNO_3$ $NaHSO_4$ Na_2SO_4	0.58 1.10 98.32	98	0.02	23.107	$NaNO_3$ $NaNO_2$	1.67 0.07	5

(a) C - weight concentrations of components in a mixture
(b) T - heating treatment temperature range
(c) C - heat treatment time
(d) φ - conversion of sodium nitrate according to reaction (2)
(e) m - mass of nitric acid into pipes
(f) m - mass of the wash-water from the trap 1
(g) η - conversion of nitric acid according to reaction (4)
(h) inert gas flow was increased in three times
(i) was used open cell with high inert gas flow; the measurement of salts concentration in the wash-water was not carried out

NO_2 liberated by the decomposition of nitric acid forms sodium nitrate and nitrite along the reaction (5):

$$2NO_2 + 2NaOH \rightarrow NaNO_3 + NaNO_2 + H_2O \quad (5)$$

Measurement of nitric acid concentration in the third trap showed that NO is not formed due to a thermal decomposition. Measurement of sodium nitrite and nitrate in the wash-waters from the first trap allows calculation of the composition of the gas mixture.

The results presented in table 3 show that $NaNO_3$ conversion substantially depends on the rate of nitric acid evacuation. Conversion of nitric acid in the vapor according to reaction (4) varies from 5 to 18 % because it strongly depends on residence time or, in other words, on flow rate of inert gas.

CONCLUSION

The present study describes one of the disposal methods of wastewater formed by organic compounds nitrosation. The reaction between $NaNO_3$, Na_2SO_4, and $NaHSO_4$ in bulk solid is studied. It is established that the exchange reaction takes place at a temperature of 150 to 240 °C in two stages, which can be explained by the formation of several phases during crystallization of salts from solution. The first stage proceeds in the temperature range from 150 to 190 °C, the second stage begins at a temperature above 200 °C, due to the presence in the structure of Na_2SO_4 the polymorphic transition. The full heat absorption of this reaction consists of two parts: the heat value of two polymorphic transitions of Na_2SO_4 - 64 $J \cdot g^{-1}$ and heat of reaction - 608 $J \cdot g^{-1}$. The study showed that the rate of reaction is defined by a rate of evacuation gaseous nitric acid. Obtained results were used in a development of industrial technology of wastewater disposal.

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