

Research Article

Studies of Recycling of Poly(vinyl chloride) in Molten Na, Ca || NO₃, OH Systems

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The interaction of poly(vinyl chloride) (PVC) with components of molten inorganic systems at the temperature range 200–500°C was studied by a combination of thermogravimetric and differential-thermal methods. The results of this study show that the melts of alkali and alkaline-earth metal nitrates can be used for utilization of wastes of halogen-containing polymeric materials. It was established that unique solid products of interaction of PVC with components of the Ca(NO₃)₂–Ca(OH)₂ mixes are ecologically safe calcium chloride and carbonate. Their formation proceeds in three stages including reactions of PVC dehydrochlorination, interactions of formed hydrocarbon residue and hydrogen chloride with calcium hydroxide and calcium nitrate, oxidation of the hydrocarbon residue, and carbonation of calcium hydroxide. A scheme for the oxidative degradation of PVC and for the binding of chlorine and carbon from the polymer in the reactions with components of Ca(NO₃)₂–NaNO₃ and Ca(NO₃)₂–Ca(OH)₂ mixtures was suggested, involving a series of consecutive and parallel reactions.

1. Introduction

Poly(vinyl chloride) has played a key role in the production of plastics for more than 40 years and occupies the second place in the production volume after polyolefins. Its use results in the formation of enormous amounts of wastes. In Western Europe, the amount of PVC in municipal wastes is estimated at approximately 2 million tons annually [1]. Incineration of municipal wastes has become an alternative to their dumping. At the same time, incineration, and especially uncontrolled incineration of wastes, leads to the pollution of the environment by the harmful substances, for example, carbon black, smoke, dioxins, acid gases, heavy metals, and aliphatic and aromatic compounds [2–5].

Molten salt oxidation is a thermal process of destroying the organic constituents of mixed wastes, hazardous wastes, and energetic materials, while retaining inorganic and hazardous constituents in the salt [6]. A possibility of using molten salts as a medium for pyrolysis was established for the first time in the disposal of used automobile tires [7]. The initial results showed that the reactions in the majority of salts were very rapid. The most widely used

media in the pyrolysis are alkali metal carbonates and chlorides and their eutectic mixtures. Chambers et al. [8] studied utilization of the organic part of scrap automobile tires in binary and ternary chloride eutectic mixtures LiCl–KCl, KCl–CuCl, NaCl–AlCl₃, LiCl–KCl–CuCl, ZnCl₂, ZnCl₂–CuCl, ZnCl₂–KCl, and ZnCl₂–SnCl₂ at 380–570°C. The nature of products and the amount of hydrogen remaining in the products were found to depend on the nature of the salts used as the pyrolysis medium. The same conclusion was made by Bertolini and Fontaine [9], who studied the pyrolysis of polyethylene, polypropylene, foamed plastic, and PVC wastes in the molten salts. They found that chlorinated plastics underwent almost complete dehydrochlorination, and that low pyrolysis temperature (420–480°C) minimized the amount of the gaseous fraction. This allowed the formation of valuable liquid and solid fractions, such as liquid petroleum fractions, aromatic compounds, solid paraffins, and monomers. Yang et al. [10] investigated the destruction of chlorinated organic solvents in a molten carbonate reactor, in which floating powdered transition metal oxides were present. The collection of chlorine in the molten salt did not change within the operating temperature range 750–950°C.

TABLE 1: Compositions of blends.

Sample no.	Composition, wt %				
	PVC	Ca(NO ₃) ₂ ·4H ₂ O	Ca(OH) ₂ ^a	NaNO ₃	NaNO ₂
1	7.45	42.97	—	49.58	—
2	19.90	20.12	59.98	—	—
3	15.85	17.95	66.20	—	—
4	17.44	58.61	23.95	—	—
5	13.75	—	48.85	—	37.40

^a86.2% Ca(OH)₂ + 13.8% CaCO₃.

In our study, we examined the oxidative degradation and pyrolysis of PVC in binary mixtures containing sodium and calcium nitrates and calcium hydroxide. Alkali metal and calcium nitrates and their eutectic mixtures are cheap, relatively low-melting materials that are stable at the temperatures up to 500°C. The presence of calcium nitrates and calcium hydroxide in the system resulted in the binding of the chlorine and carbon of the polymer into calcium chlorides and carbonates, respectively [11]. Also, PVC stabilized with K(Na)NO₃ exhibited good thermal stability within the temperature interval of 140–200°C [12]. Griffiths et al. [13] proposed that the concentration of the oxidizing species, superoxide, and peroxide ions, produced from the oxygen included in the carbonate melt, could be increased and maintained at a certain level by the addition of nitrate ions as a catalyst. Thus, molten carbonate-nitrate system provides the most efficient oxidizing conditions currently known. However, we found no data in the literature on the use of molten nitrates for disposal of plastic wastes, including those containing chlorine.

2. Experimental

2.1. Materials. The powder of emulsion PVC of grade E-6250Zh of $d = 1.4 \text{ g/cm}^3$ and viscosity of 0.68 cp, chemically pure grade sodium and calcium nitrates, and pure grade calcium hydroxide were supplied by Volzhskii Promyshlennyi kompleks (Volzhsk, Russia). The blends of PVC with inorganic components were prepared by stirring them as suspension in acetone during 10 min. The compositions of the blends are given in Table 1.

2.2. Thermogravimetry. The thermal behavior of the blends was studied by differential thermal analysis in combination with thermal gravimetric analysis using Paulik, Paulik, and Erdei Q-1500D thermal analyser, in alundum crucibles at a heating rate of 5°C/min in air. The weight of the samples was 0.1 g.

2.3. Processing of Blend Samples at Constant Temperature and Product Analysis. The sample of the blend was placed in a quartz ampoule and introduced into the furnace equipped with an appropriate thermocouple and a temperature control system. The fixed temperatures were preset in an interval of 230–330°C. The content of the formed metal chlorides was determined by capillary electrophoresis with an Agilent G1600 AX device after dissolving the mixture in

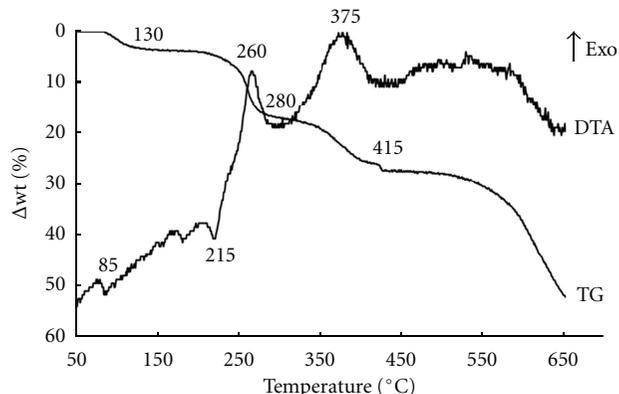


FIGURE 1: TG and DTA curves for PVC-[Ca(NO₃)₂ + NaNO₃](eut.) blend.

distilled water. The amount of calcium carbonate formed was determined by the procedure described in [14]. The carbon and hydrogen content in the residues after pyrolysis was determined with a CHNS-932 analyzer (LECO). The relative amount of the chlorine (α_{Cl}) or carbon (α_{C}) bound was calculated as the ratio of the weight of chlorine or carbon in formed metal chloride ($\text{wt}_{\text{Cl}}(\text{MCl})$) or carbonate ($\text{wt}_{\text{C}}(\text{MCO}_3)$) to the weight of chlorine ($\text{wt}_{\text{Cl}}(\text{PVC})$) or carbon ($\text{wt}_{\text{C}}(\text{PVC})$) in the starting PVC:

$$\alpha_{\text{Cl}} = 100\% \cdot \frac{\text{wt}_{\text{Cl}}(\text{MCl})}{\text{wt}_{\text{Cl}}(\text{PVC})}, \quad \alpha_{\text{C}} = 100\% \cdot \frac{\text{wt}_{\text{C}}(\text{MCO}_3)}{\text{wt}_{\text{C}}(\text{PVC})}. \quad (1)$$

3. Results and Discussion

We found that the Ca(NO₃)₂-NaNO₃ mixture of the eutectic composition, when heated, lost crystallization water at 110°C and then melted at 220°C, and at 505°C, calcium nitrate started to decompose. When the blend of PVC with Ca(NO₃)₂-NaNO₃(eut.) (sample no. 1) was heated, the exothermic events were observed, with maxima at 260 and 375°C after melting of the eutectics (Figure 1). The TG profile showed the weight-decreasing transitions at these temperatures. The weight of the sample after removal of crystallization water is 96.99 mg, and it contained (mg) PVC—7.47, NaNO₃—49.73, and Ca(NO₃)₂—39.79. An analysis for soluble chlorine in the residue after heating to 500°C showed that 35.1% of the PVC chlorine was bound into a soluble chloride. No carbonate ions were detected in the solution, indicating that the PVC carbon was not bound.

Basing on the weight losses in the separate steps of the process, and based on the overall material balance, we suggest a two-step mechanism for the process. In the first step, starting from 200°C, PVC undergoes thermal decomposition with the release of HCl. This process propagates along the polymer chain and yields polyenes [15, 16]. As a result, a carbon-rich residue with a high reducing power is formed.

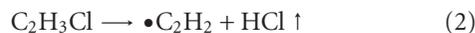
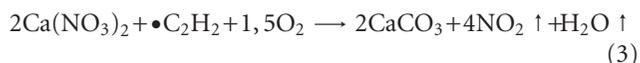


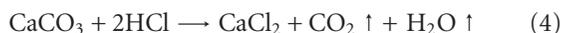
TABLE 2: Weight change of the starting substances and the solid reaction products during the heating of $\text{Ca}(\text{NO}_3)_2\text{-NaNO}_3(\text{eut.}) + \text{PVC}$ blend and the heats of reactions (2)–(4).

Reaction	Weight change of the starting substances and the solid reaction products Δm , mg					$\sum \Delta m$, mg	$-\Delta H$, J
	PVC	$\bullet\text{C}_2\text{H}_2$	$\text{Ca}(\text{NO}_3)_2$	CaCO_3	CaCl_2		
(2)	-7,47	+ 3,11				-4,36	12,3
(3)		-3,11	-39,23	+ 23,92		-18,42	111,2
(4)				-2,09	+ 2,33	+ 0,24	0,8
					Total	-22,54	

Simultaneously, reduction of calcium nitrate starts in accordance with the overall reaction (3), consisting, possibly, on the two rapid processes (3a) and (3b):



Almost all of the calcium nitrate is thus reacted. At the second step, hydrogen chloride formed in process (2) reacts with calcium carbonate to form the final product, calcium chloride:



Weight changes for the starting substances and the solid reaction products that occurred during the heating of $\text{Ca}(\text{NO}_3)_2\text{-NaNO}_3(\text{eut.}) + \text{PVC}$ blend are shown in Table 2. We took into account that only 35.1% of the hydrogen chloride reacted with calcium carbonate.

Table 2 also contains the calculated values of the heats of reactions, indicating that each stage and the process in general are exothermic over the interval of temperatures studied.

The total decrease in the weight of the sample in the range of temperatures 200–415°C was 22.54 mg, which matched the weight loss of the sample on the TG curve of 22.65 mg. This match confirms the proposed mechanism of the interactions in the system. Reaction (2) should occur first, and reactions (3) and (4) follow in parallel, with participation of both products of reaction (2). Due to the simultaneous occurrence of several reactions in the system, it is impossible to allocate temperature intervals of the separate stages of the process.

The correlation between the relative amount of PVC chlorine that is converted into soluble chlorides (α_{Cl}) and chlorine content in the solid residue during isothermal heating of the blend during 60 min is shown in Figure 2.

A sharp increase of α_{Cl} is observed at a temperature of 230°C, and α_{Cl} increases to 68.6% at 280°C. At the same time, the chlorine content in the solid residue decreases from 7.5% at 230°C to 0.9% at 280°C. Thus, under these conditions, about 30% of chlorine passes in a gas phase, most likely in the form of HCl.

To elucidate the role of nitrates in binding of the polymer chlorine, we studied the processes occurring during the

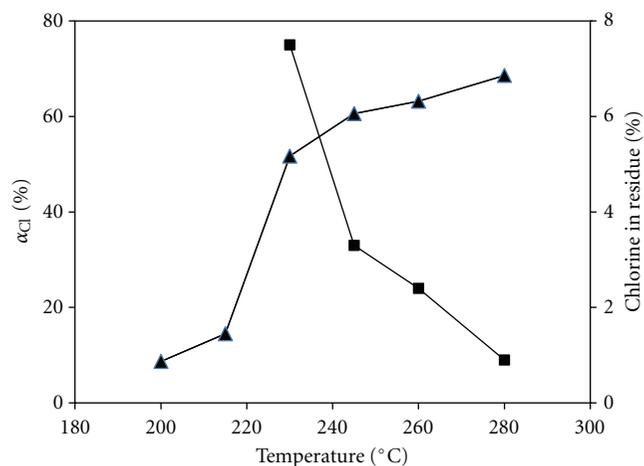


FIGURE 2: Correlation between the relative amount of PVC chlorine converted into soluble chlorides (α_{Cl}) and the chlorine content in the solid residue.

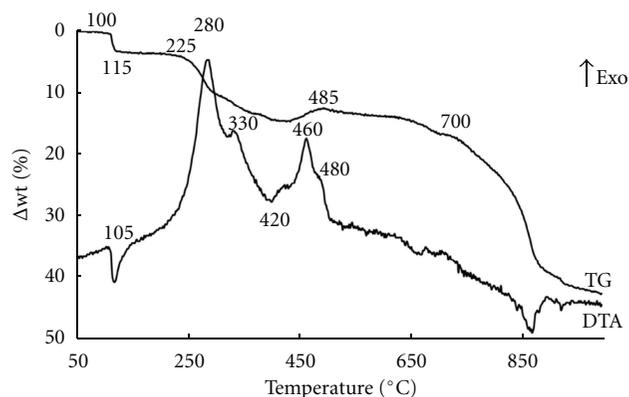


FIGURE 3: TG and DTA curves for the $\text{PVC-Ca}(\text{NO}_3)_2\text{-Ca}(\text{OH})_2$ blend.

heating of $\text{Ca}(\text{NO}_3)_2\text{-Ca}(\text{OH})_2\text{-PVC}$ blend (samples no. 2–4). The weight variation pattern, thermal events, and their maxima in the temperature range 20–600°C were essentially the same as for the $\text{Ca}(\text{OH})_2\text{-PVC}$ blend [17]: weight loss in the range of 225–420°C followed by the weight gain on further heating to 485°C, with three exothermic events with maxima at 285, 330, and 460°C (Figure 3). Calcium chloride was formed when the mixtures were heated above 225°C, and by 500°C, the total amount of PVC chlorine was converted to

TABLE 3: Weight change of the starting substances and the solid reaction products during the heating of $\text{Ca}(\text{NO}_3)_2$ - $\text{Ca}(\text{OH})_2$ -PVC blend and the heats of reactions (6), (9), (10), and (13).

Reaction	Weight change of starting solid substance and reactions products Δm , mg						$\sum \Delta m$, mg	$-\Delta H$, J
	PVC	$\bullet\text{C}_2\text{H}_2$	$\text{Ca}(\text{NO}_3)_2$	CaCO_3	CaCl_2	$\text{Ca}(\text{OH})_2$		
(6)	-20,18	+ 8,39			+ 17,93	-11,95	-5,81	11,6
(9)		-2,64	-16,68	+ 20,34		-7,52	-6,50	113,1
(10)		-5,75					-5,75	290,4
(13)				+ 44,20		-32,71	+ 11,49	30,8
						Total	-6,57	

a soluble chloride. The analysis of the residue after heating to lower temperatures showed that calcium carbonate was formed in the temperature range of 280–400°C.

In contrast to the $\text{Ca}(\text{NO}_3)_2$ - NaNO_3 (eut.) + PVC blend, the residue after heating contained calcium carbonate formed in the temperature range of 330–485°C. The relative amount of carbon bound α_C was 64–71% and α_{Cl} 64–89%, which is comparable with the values obtained for the $\text{Ca}(\text{OH})_2$ -PVC system [17].

α_{Cl} decreases with a decrease in the calcium hydroxide content. For example, after heating sample no. 4 to 400°C, α_{Cl} is equal to 31%. Thus, calcium hydroxide plays a major role in binding of the chlorine from PVC.

Replacement of calcium nitrate in the blend by a stronger oxidant, sodium nitrite (sample no. 5), leads to a considerable increase of the degree of binding of chlorine and carbon from PVC. After isothermal heating of the sample at 330°C for 20 min, α_{Cl} and α_C are 99 and 83%, respectively.

Performing a material balance in combination with the elemental analysis and measurement of the product amounts permits the distinction of separate stages of the process.

Weight of the sample after removal of crystallization water is 97.39 mg, and it contained (mg), PVC—20.18, $\text{Ca}(\text{OH})_2$ —52.18, $\text{Ca}(\text{NO}_3)_2$ —16.68, and CaCO_3 —8.35. The weight change of the weight of starting substances and the solid reaction products are shown in Table 3.

At a stage I in the range of temperatures 225–330°C, reactions (2) and (5) consistently proceed

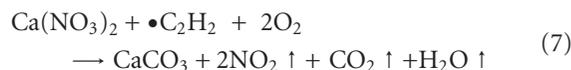


Assuming that the whole quantity of the PVC reacts and all the produced hydrogen chloride is converted to calcium chloride, by summarizing the equations of reactions (2) and (5), we obtain

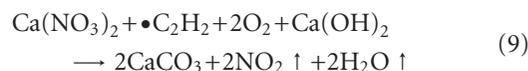


Reducing of the weight of the sample at this stage, 5,81 mg well coincides with loss of the weight 5,72 mg calculated thermogravimetrically. Composition of the residue I (mg) is $\text{Ca}(\text{OH})_2$ —40,23; CaCl_2 —17,93; $\bullet\text{C}_2\text{H}_2$ —8,39; CaCO_3 —8,35; $\text{Ca}(\text{NO}_3)_2$ —16,68.

At a stage II in the range of 330–400°C, reactions (7) and (8) consistently proceed



Summarizing (7), (8), we obtain



The weight loss of the sample at stage II, 6,50 mg, coincided with the value of 5,98 mg determined thermogravimetrically. Composition of the residue II was (mg) $\text{Ca}(\text{OH})_2$ —32,71; CaCl_2 —17,93; $\bullet\text{C}_2\text{H}_2$ —5,75; CaCO_3 —28,69. According to the elemental analysis, the residue contained 9,38 wt% of carbon and 0,77 wt% of hydrogen. Theoretically the content of C and H in the residue should be 10,22 and 1,55 wt%, respectively. The difference between the measured and theoretical values indicates that partial decomposition of $\text{Ca}(\text{OH})_2$ and partial oxidation of $\bullet\text{C}_2\text{H}_2$ have occurred.

At stage III, in the temperature range of 400–500°C the oxidation reactions of the hydrocarbon residue (10) and dehydration of calcium hydroxide (11) appeared to proceed in parallel



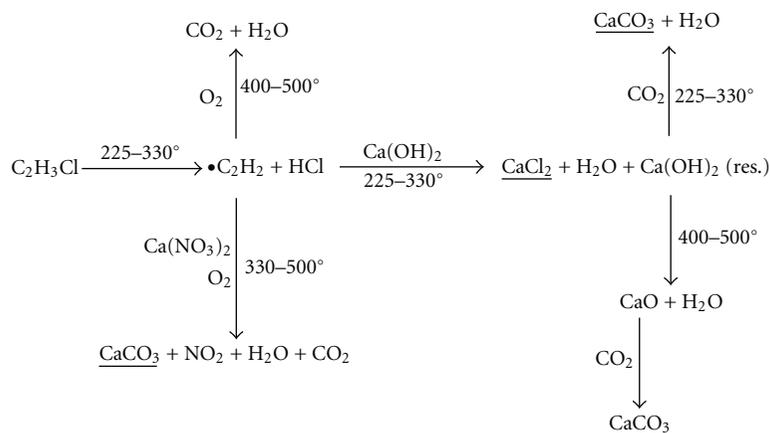
The carbon dioxide formed as a result of reaction (10) reacted with calcium oxide formed in reaction (11)



Summarizing (11) and (12), we obtain



The weight change of the sample at stage III, +5,74 mg, was slightly more than a gain of weight of 3,22 mg, determined thermogravimetrically. This indicates the incomplete interaction of carbon dioxide with calcium oxide despite the fact that the quantity of reactants is stoichiometric. Composition of residue III was (mg) CaCl_2 —17,93, CaCO_3 —20,34 + 44,20 + 8,35 = 72,89. The theoretical weight of the residue



SCHEME 1

17,93 + 72,89 = 90,86 mg differs from that determined by thermogravimamm 87,59 mg due to the reasons mentioned above.

Thus, for the system $\text{Ca(NO}_3)_2$ – Ca(OH)_2 –PVC during heating over the interval 20–500°C, it is possible to suggest the following reaction Scheme 1 (the final solid products of reactions are underlined).

4. Conclusions

The interaction of poly(vinyl chloride) with the components of molten inorganic systems in the temperature range of 200–500°C was studied by a combination of thermogravimetric and differential-thermal analysis. The results of this study show that the melts of alkali and alkaline-earth metal nitrates can be used for the recycling of wastes of halogen-containing polymeric materials. It was established that the solid products of the interaction of PVC with the components of the $\text{Ca(NO}_3)_2$ – Ca(OH)_2 mixtures are ecologically safe calcium chloride and calcium carbonate. Their formation occurs in three stages: dehydrochlorination of PVC, interactions between the resulting hydrocarbon residue and hydrogen chloride with calcium nitrate and calcium hydroxide respectively, and the oxidation of the hydrocarbon residue and carbonation of calcium hydroxide.

A possible mechanism was suggested for the binding of chlorine and carbon from the polymer in the reactions with components of $\text{Ca(NO}_3)_2$ – NaNO_3 and $\text{Ca(NO}_3)_2$ – Ca(OH)_2 mixtures.

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References

- [1] R. Zevenhoven, M. Karlsson, M. Hupa, and M. Frankenhäuser, "Combustion and gasification properties of plastics particles," *Journal of the Air and Waste Management Association*, vol. 47, no. 8, pp. 861–870, 1997.
- [2] K. Everaert and J. Baeyens, "The formation and emission of dioxins in large scale thermal processes," *Chemosphere*, vol. 46, no. 3, pp. 439–448, 2002.
- [3] F. W. Karasek and O. Hutzinger, "Dioxin danger from garbage incineration," *Analytical Chemistry*, vol. 58, no. 6, pp. 633A–642A, 1986.
- [4] D. Lanoir, G. Trouvé, and L. Delfosse, "Laboratory scale studies on gaseous emissions generated by the incineration of an artificial automotive shredder residue presenting a critical composition," *Waste Management*, vol. 17, no. 8, pp. 475–482, 1998.
- [5] I. C. McNeill, L. Memetea, and W. J. Cole, "A study of the products of PVC thermal degradation," *Polymer Degradation and Stability*, vol. 49, no. 1, pp. 181–191, 1995.
- [6] P. C. Hsu, K. G. Foster, T. D. Ford et al., "Treatment of solid wastes with molten salt oxidation," *Waste Management*, vol. 20, no. 5–6, pp. 363–368, 2000.
- [7] J. W. Larsen and B. Chang, "Conversion of scrap tires by pyrolysis in molten salts," *Rubber Chemistry and Technology*, vol. 49, no. 4, pp. 1120–1128, 1976.
- [8] C. Chambers, J. W. Larsen, W. Li, and B. Wiesen, "Polymer waste reclamation by pyrolysis in molten salts," *Industrial & Engineering Chemistry Process Design and Development*, vol. 23, no. 4, pp. 648–654, 1984.
- [9] G. E. Bertolini and J. Fontaine, "Value recovery from plastics waste by pyrolysis in molten salts," *Conservation and Recycling*, vol. 10, no. 4, pp. 331–343, 1987.
- [10] H. C. Yang, Y. J. Cho, H. C. Eun, J. H. Kim, and Y. Kang, "Destruction of chlorinated organic solvents in a molten carbonate with transition metal oxides," *Studies in Surface Science and Catalysis*, vol. 159, pp. 577–580, 2006.
- [11] A. A. Fedorov, Y. S. Chekryshkin, O. V. Rudometova, and Z. A. Vnutskikh, "Application of inorganic compounds at the thermal processing of polyvinylchloride," *Russian Journal of Applied Chemistry*, vol. 81, no. 9, pp. 1673–1685, 2008.
- [12] G. Stoev, D. Uzunov, and T. Dentchev, "Studies on the stabilization of poly(vinyl chloride) with a stabilizer containing

- nitrate compounds,” *Journal of Analytical and Applied Pyrolysis*, vol. 16, no. 4, pp. 335–343, 1989.
- [13] T. R. Griffiths, V. A. Volkovich, and W. R. Carper, “The structures of the active intermediates in Catalyst-Enhanced Molten Salt Oxidation and a new method for the complete destruction of chemical warfare arsenicals,” *Structural Chemistry*, vol. 21, no. 2, pp. 291–297, 2010.
- [14] Z. A. Vnitskikh, E. A. Zhilkina, L. D. Asnin, and A. A. Fedorov, “Definition of carbonates in small weight samples with use of a gas chromatography method,” *Zavodskaya Laboratorija. Diagnostika Materialov*, vol. 68, no. 8, pp. 19–20, 2002 (Russian).
- [15] E. P. Chang and R. Salovey, “Pyrolysis of poly(vinyl chloride),” *Journal of Polymer Science*, vol. 12, no. 12, pp. 2927–2941, 1974.
- [16] A. Guyot and M. Bert, “Sur la dégradation thermique du polychlorure de vinyle. VI. Etapes initiales—étude générale préliminaire,” *Journal of Applied Polymer Science*, vol. 17, no. 3, pp. 753–768, 1973.
- [17] O. V. Rudometova, Z. A. Vnitskikh, A. A. Fedorov, and Y. S. Chekryshkin, “Interaction of polyvinylchloride with calcium and magnesium hydroxides,” *Khimicheskaja Technologija*, vol. 9, no. 8, pp. 367–372, 2008 (Russian).



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