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Utilization of chloroorganic waste by their catalytic copolymerization

Summary — A new method, proposed by authors, of utilization of chloroorganic waste accompanying the production of 1,2-dichlorethane consists in alkaline dehydrochlorination of this waste (equations 1—5) and simultaneous copolymerization with the unsaturated hydrocarbons of C_5—C_9 fraction. At the first stage of the process at ambient temperatures (≤ 50 °C) ionic polymerization and copolymerization of the non-saturated components, take place. Then, at higher temperatures (> 50 °C) the free radical homopolymerization and copolymerization of vinyl chloride and vinylidene chloride most probably proceed. As a final product, oligomeric and polymeric resin-like products are formed, which can be recommended for the use as hydroisolating material.

Key words: chloroorganic waste, alkaline dehydrochlorination, copolymerization, homopolymerization.

UTYLIZACJA ODPADÓW CHLOROORGANICZNYCH METODĄ ICH KATALITYCZNEJ KOPOLIMERYZACJI

Streszczenie — Zaproponowana przez autorów nowa metoda utylizacji odpadów chloroorganicznych towarzyszących produkcji 1,2-dichloroetanu polega na alkalicznym odchlorowodorowaniu tych odpadów (równania 1—5) i jednoczesnej kopolimeryzacji z frakcją nienasyconych węglowodorów C_5—C_9. W pierwszej fazie procesu, w temperaturze otoczenia (≤ 50 °C) ma miejsce polimeryzacja jonowa i kopolimeryzacja nienasyconych składników. W temperaturze wyższej (> 50 °C), zachodzi prawdopodobnie wolnorodnikowa homopolimeryzacja i kopolimeryzacja chlorku winylu i chlorku winylidenu. W wyniku tych reakcji powstają oligomerowe i polimerowe, podobne do żywic produkty, które mogą być rekomendowane jako materiały hydroizolacyjne.

Słowa kluczowe: odpady chloroorganiczne, alkaliczne odchlorowodorowanie, kopolimeryzacja, homopolimeryzacja.

An industrial production of chloroorganic substances has been continuously increasing during last 40 years. The world production of chloroorganic substances exceeds 30 mln tons per year. This situation results in the continuous increase of a quantity of the chloroorganic waste (COW) formation. In the world scale a quantity of waste is estimated in millions of tons. The most serious problem is created by the waste accompanying the chlorinated polymers production, the quantity of which is 10 mln tons per year, and industrial waste accompanying low molar mass chloroorganic compounds productions — approximately 1,5 mln tons per year [1]. The industrial COW is dangerous in the ecological meaning, whereas the chlorinated polymers at the normal conditions are non- or low toxic. The utilization of COW is complicated because of its high chemical stability and toxicity it contains the compounds mainly of the 1—2 class of danger, and also of high price of equipment which is used for its utilization.

Two major methods of utilization of COW are mentioned in the scientific literature combustion and burial. These methods are most widespread in industry, because they are simple and nonexpensive.

The combustion can not be economically profitable, because all chloroorganic solid and gaseous substances are lost. In the case of combustion of COW the toxic compounds, which could contaminate an atmosphere, are also formed. Available data show that during processes of combustion of COW phosgene, dioxins, or dioxins derivatives are formed [2, 3].

Though the constant work at the improvement of combustion methods is conducted, it seems that COW burning is possible only temporarily, till more ecologically safe methods will be developed. For example only the oxygenless methods of processing could guarantee the full absence of dioxins [3]. Unfortunately, in our opinion, the ecological safety is not a decisive factor in using a given utilization method in industry — more important is its economical profitability.

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Thus, in the present paper we describe the method, which is based on alkaline dehydrochlorination of chloroorganic waste with simultaneous copolymerization of COW with olefins that are produced at the "Lukor" (Kalush, Ukraine) chemical complex plant. The olefin by-products consist of the C_5—C_9 fraction, obtained by means of fractionating distillation of pyrogas while cooling and compressing in the department of pyrolysis. This fraction contains 50—64 wt. % of valuable dienes, such as isoprene, cyclopentadiene, pentadienes, and butadiene).

EXPERIMENTAL

Materials

In the process of production of 1,2-dichloroethane and vinyl chloride in the chemical complex "Lukor" the dichloroethane is synthesized by means of a direct and oxidative chlorination of ethylene. A range of the chloroorganic and organic wastes, appearing at the stage of rectification is given in table 1. They are formed because of some side reactions and adventitiously present impurities in the starting material. The total quantity of waste at the overloaded capacity department can run up to 6750 tones per year.

Table 1. Chemical composition of the chloroorganic waste (COW) and organic waste expressed in wt. %

1,2-dichloro-ethylene	1,1-dichloro-ethane	Benzene	Trichloro-ethylene	1,2-dichloro-ethane	Perchloro-ethylene	1,1,2-trichloro-ethane	Σ others
2.7—3	6.8—10	0.1—0.5	1.2—3	18—30	3.3—5	30—40.25	37.9—8.25

Table 2. General characteristics of the C_5—C_9 fraction used

Parameter	Norm
Starting boiling temperature, °C	30
Final boiling temperature, °C	200
Resin content, ppm	up to 500
Water amount, wt. %	0.05
Chlorine content, wt. %	up to 0.002
Sulfur content, wt. %	up to 0.1
Density, kg/m^3	670—730
Bromide number, Br_2/100 g of product	100—180

The unsaturated C_5—C_9 fraction (Table 2), containing 20—25 wt. % of isoprene, 20—25 wt. % of cyclopentadiene, 10—14 wt. % of pentadienes and butadiene, and 50—36 wt. % of other olefins is a by-product which is formed in the "Lukor" plant during the pyrolysis of a diesel fuel. It is collected as a distillate during the pyrogas separation. Classes of danger and maximum permissible concentration (MPC) of components of this fraction in the air of working area are listed in table 3.

Table 3. Classes of danger of COW reagents

Material	Class of danger (toxicity level)	MPC, mg/m^3
Dichloroethane	2	10
Trichloroethane	2	20
Vinylchloride	1	1
Vinylidenchloride	2	40

Process description

First, the alkaline dehydrochlorination of the chloroorganic waste [4] was carried out. During this process the following reactions occur:

$$2CH_2Cl–CH_2Cl + Ca(OH)_2 \rightarrow 2CH_2{=}CHCl + CaCl_2 + 2H_2O \tag{1}$$

$$2CH_2Cl–CHCl_2 + Ca(OH)_2 \rightarrow 2CH_2{=}CCl_2 + CaCl_2 + 2H_2O \tag{2}$$

$$CH_2Cl–CHCl_2 + NaOH \rightarrow CH_2{=}CCl_2 + NaCl + H_2O \tag{3}$$

$$ClCH_2–CH_2Cl + NaOH \rightarrow CH_2{=}CHCl + NaCl + H_2O \tag{4}$$

$$CH_2{=}CHCl + NaOH \rightarrow CH{\equiv}CH + NaCl + H_2O \tag{5}$$

Dehydrochlorination was conducted using the laboratory set which consists of a four-neck round-bottom flask, put in the thermostat, dripping hopper for the supply of COW, reversing condenser, special miner and pipe for the supply of N_2. This process takes 3.5—4.5 h at the temperature 77—80 °C and under N_2 atmosphere. Dehydrochlorination was conducted with all of the industrial safety rules because its products such as vinyl or vinyliden chlorides are very reactive and toxic (their boiling temperatures are equal to 13.4 and 37 °C, respectively).

At the second stage the newly formed monomers (vinyl and vinyliden chlorides) and the unreacted COW (depleted mostly of trichloroethylene) were copolymerized with the unsaturated C_5—C_9 fraction.

The copolymerization was conducted in organic solvents such as xylene, toluene, heptane, CCl_4 or diphenylamine (DiphAm) and in the temperature range from 15 to 60 °C; $AlCl_3$ was employed as a catalyst. In order to prevent hydrolysis of the catalyst the maximum content of moisture in COW must not exceed 200 ppm. Conversion of COW and C_5—C_9 fraction to polymer (in percent) was determined. For that purpose COW and C_5—C_9 fraction before reaction and residue of these components after reaction were weighed.

RESULTS AND DISCUSSION

The experimental results are summarized in Table 4.

T a b l e 4. Results of catalytic copolymerization products of alkaline dehydrochlorination of chloroorganic waste with the unsaturated fraction C_5—C_9

Solvent	COW/C_5—C_9 fraction ratio	COW/solvent volume ratio	Content of $AlCl_3$, wt. %	Temperature of copolymerization, °C	Conversion of COW, %	Yield soluble resin, wt. %	Yield insoluble resin, wt. %
Xylene	0:1	3:1	5	50	100	99	1
Xylene	1:1	3:1	8	50	100	75	25
Xylene	1:1	3:1	7	50	95	85	15
Xylene	1:1	3:1	6	50	89	96	4
Xylene	1:1	3:1	4	50	77	99	1
Xylene	1:1	5:1	5	50	66	97	3
Xylene	1:1	4:1	5	50	78	99	1
Xylene	1:1	2:1	5	50	91	88	12
Xylene	1:1	3:1	5	15	84	99	1
Xylene	1:1	3:1	5	30	85	99	1
Xylene	1:1	3:1	5	60	87	89	11
Xylene	4:1	3:1	5	50	50	98	2
Xylene	3:1	3:1	5	50	56	98	2
Xylene	2:1	3:1	5	50	67	99	1
Xylene	1:1	3:1	5	50	85	99	1
Xylene	1:1,5	3:1	5	50	97	99	1
Xylene	1:2	3:1	5	50	100	99	1
Toluene	1:2	3:1	5	50	100	99	1
Heptane	1:2	3:1	5	50	64	55	45
CCl_4	1:2	3:1	5	50	37	12	88
DiphAm[a)]	1:2	3:1	5	50	—	—	—
Xylene	1:2	3:1	5	50	66	73	27
Xylene[b)]	1:2	3:1	5	50	34	61	39

[a)] DiphAm — diphenylamine; process conducted over $FeCl_2$ as a catalyst. [b)] Process conducted with $ZnCl_2$ as a catalyst.

Figure 1 shows dependence of the joint conversion of COW and C_5—C_9 fraction (for COW/C_5—C_9 fraction = 1/1 v/v, COW/solvent = 3/1 v/v and T = 50 °C) on the concentration of the catalyst. The conversion increases from 78 to 100 % with increasing of the catalyst concentration from 1 to 8 wt. %. This kind of dependence can be explained by deactivation of the catalyst caused by the hydrolysis, particularly effective for the lower catalyst content. At or above 8 wt. % of $AlCl_3$ in the feed practically all water is being removed from the system.

The influence of temperature on the joint conversion of COW and C_5—C_9 fractions (for COW/C_5—C_9 fraction = 1/1 v/v, COW/solvent = 3/1 v/v and 5 wt. % of $AlCl_3$) is shown in the Figure 2. The increase of temperature from 15 to 65 °C gives a slight acceleration of the copolymerization which is reflected in the increase of conversion from 84 to 87 % in this range of temperatures. The explanation of this phenomenon could be the ionic mechanism of the copolymerization in which propagation rate increase is counterbalanced at higher temperatures by an appearance of the undesired side reactions such as proton abstraction, leading to termination.

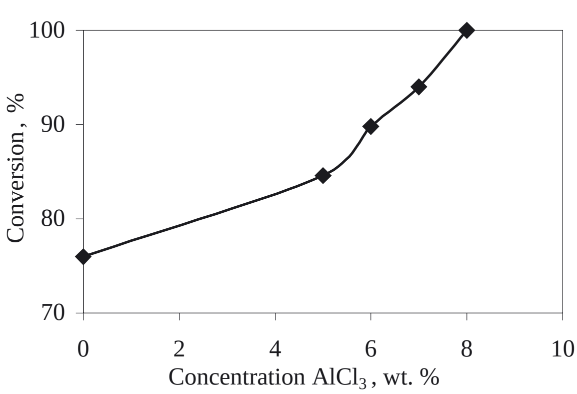

Fig. 1. Dependence of the COW and C_5—C_9 joint conversion on the $AlCl_3$ catalyst concentration (COW/C_5—C_9 fraction = 1/1 v/v, COW/solvent = 3/1 v/v, xylene solvent, T = 50 °C)

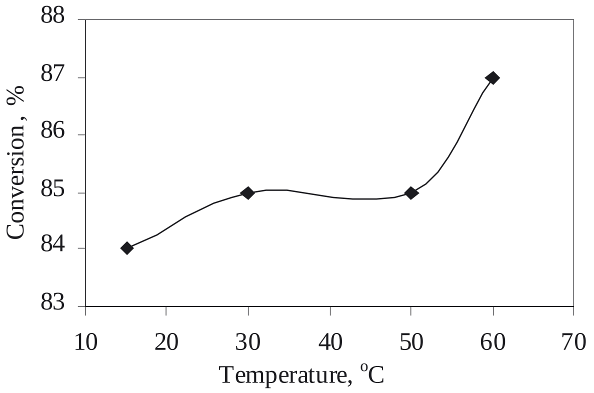

Fig. 2. Dependence of the COW and C_5—C_9 joint conversion on the copolymerization temperature (COW/C_5—C_9 fraction = 1/1 v/v, COW/solvent = 3/1 v/v, 5 wt. % of $AlCl_3$, xylene solvent)

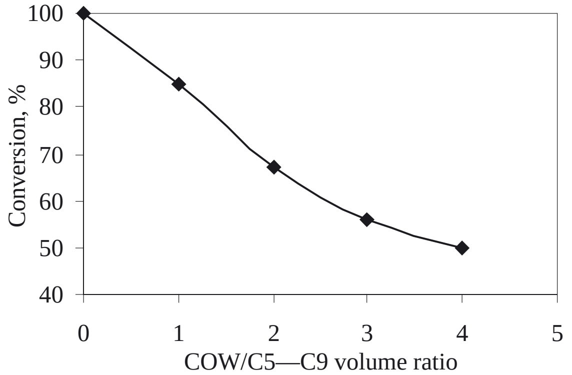

Fig. 3. Dependence of the COW and C_5—C_9 joint conversion on their volume ratio (COW/solvent = 3/1 v/v, 5 wt. % of $AlCl_3$, xylene solvent, T = 50 °C)

The COW and C_5—C_9 weight ration also influenced on the their joint conversion. Figure 3 shows that the increase of COW content with regard to the C_5—C_9 content in the feed (for COW/solvent = 3/1 v/v, 5 wt. % of CCl_3 and T = 50 °C) leads to the decrease of both reagents conversion from 100 to 50 %. This behavior can be explained by the higher reactivity of the C_5—C_9 fraction in comparison to that of COW since in the former are diene hydrocarbons present.

From the results presented in table 4 we can conclude that COW/solvent volume ratio also strongly influenced on conversion. The highest value of conversion we obtained for COW/solvent = 2/1 v/v.

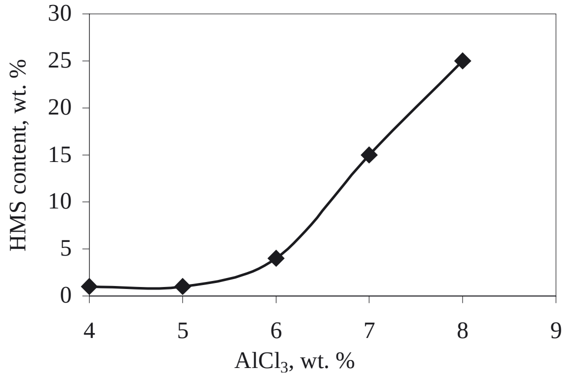

Fig. 4. Dependence of the insoluble high-molecular substances (HMS) content in the products on $AlCl_3$ catalyst concentration (COW/C_5—C_9 fraction = 1/1 v/v, COW/solvent = 3/1 v/v, xylene solvent, T = 50 °C)

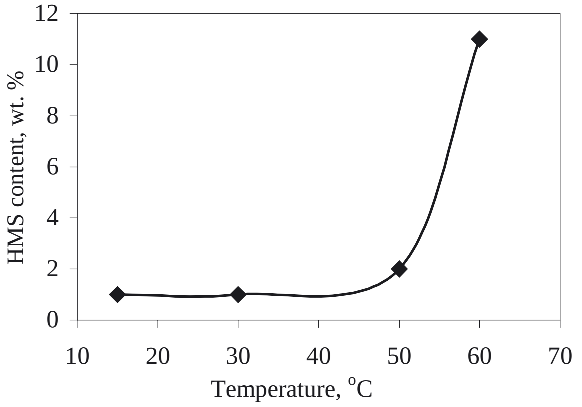

Fig. 5. Dependence of the insoluble resin yield in the products mixture on the copolymerization temperature (COW/C_5—C_9 fraction = 1/1 v/v, COW/solvent = 3/1 v/v, 5 wt. % of $AlCl_3$, xylene solvent)

Moreover, we observed the insoluble (in organic solvents used), high-molecular substances (HMS) formation apart from the soluble polymers and oligomers. We studied extent of these HMS formation on the catalyst content (Figure 4) and the copolymerization temperature (Figure 5). As it stems from Figs. 4 and 5 content of HMS in the products mixture, at the applied copolymerization conditions, did not exceed 25—30 %. In our opinion, HMS consists mostly of poly(vinyliden chloride) and poly(vinyl chloride) which are insoluble in the reacting mixture. However formation of the crosslinked polymers can not be also excluded, particularly at the higher temperatures favoring the free radical reactions.

CONCLUSIONS

By changing practically all regime parameters of the process consisting of alkaline dehydrochlorination of the chloroorganic waste (COW) followed by the copolymerization with the C_5—C_9 unsaturated hydrocarbons fraction the optimum conditions of this process have been established:

— COW and C_5—C_9 volume ratio: from 1/1 to 1/2,
— COW and the aromatic solvent volume ratio: from 2/1 to 3/1,
— $AlCl_3$ catalyst concentration: 5-8 wt. %,
— temperature: 60—70 °C.

On the initial stages of the copolymerization and at lower temperatures the ionic mechanism most probably prevail, whereas at higher temperatures the radical homo- and copolymerization starts to operate. Eventually, oligomeric and the high-molecular weight resin-like products are formed.

The elaborated by us synthetic route of the joint simultaneous utilization of the chloroorganic and the olefin production by-products creates a possibility to process these wastes into the useful products. Their potential application includes for example the hydroisolating materials area.

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W kolejnym zeszycie ukażą się m.in. następujące artykuły:

— Problematyka krystalizacji polimerów w procesie wtryskiwania
— Wtryskiwanie tworzyw polimerowych wspomagane wodą oraz układem gaz + woda
— Aspekty projektowania i wytwarzania mikroelementów oraz zastosowanie technologii mikrowtryskiwania
— Wtryskarki elektryczne
— Stereokompleksy poli (*R*)- i poli (*S*)-laktydów gwiaździstych zawierających różną liczbę ramion. Synteza i właściwości termiczne (*j. ang.*)
— Wykres sieciowania czas-temperatura-przemiana (TTT) dla układu epoksydowego EPY® (*j. ang.*)
— Właściwości termiczne i dielektryczne niektórych kompozycji epoksydowych
— Mechanochemiczny recykling kauczuku naturalnego wulkanizowanego za pomocą siarki (*j. ang.*)