Analytical and Physical Investigation of Alkyd Resin in the Course of its Preparation. I. Determination of Composition of Reaction Mixture Using Volatile Monocarboxylic Acid for Alkyd Synthesis

ALOIS KAŠTÁNEK, KAREL HÁJEK, and OldŘICH DUFKA, *Research Institute for Synthetic Resins and Lacquers, Pardubice, Czechoslovakia*

Synopsis

The extent of esterification between isocaprylic acid, phthalic anhydride, glycerol, and pentaerythritol was followed by analysis of reaction mixture. Acid numbers, hydroxyl numbers, and saponification numbers of alkyd samples were determined at different stages of the reaction. A way of calculation of the losses of volatile monomer reactants from liquid reaction mixture was proposed. The amounts of condensed water experimentally measured during alkyd synthesis correspond to the amounts of water losses from the batch that were calculated.

INTRODUCTION

In the course of preparation of alkyd resins, esterification occurs between carboxylic acids or their derivatives and polyalcohols.[1-3] The carboxylic acids are mostly represented by unsaturated monocarboxylic acids prepared by splitting the vegetable oils and dicarboxylic acids derivated from benzene. Most frequently used polyalcohols are glycerol and pentaerythritol. Besides the main esterification reaction, side reactions can occur, for example, decarboxylation, etherification, polymerization between chains of unsaturated fatty acids, etc.[4,5]

The results of study of the extent of esterification reaction between isocaprylic acid, phthalic anhydride, glycerol, and pentaerythritol are given in this paper. Use of isocaprylic acid secures elimination of polymerization that occurs when unsaturated monocarboxylic acids are used. Boiling point of isocaprylic acid is 224°C, so that isocaprylic acid is partly present in vapor phase above the liquid reaction mixture at reaction temperature. As well, glycerol can be partly present in the vapor phase. It is necessary to take account of volatility of these reactants, and their losses from the reaction mixture must be involved into balance calculations.

THEORETICAL

If some volatile reactants for preparation of alkyd resin are used, it is necessary to arrange processes in such a way that losses of volatile components are as small as possible. That is why a back column is joined to the reaction flask. The vapors of monomer reactants that left the hot liquid reaction mixture condense in the column, whereas the water vapors con-

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dense only in a water-cooled condenser attached beyond the column. So, a portion of monomer components is away from the liquid batch during alkyd synthesis, and it is necessary to take account of this fact when the extent of esterification reaction is investigated. The way of calculation of real content of reactants in the batch is given here, so that it is possible to eliminate the errors arising from neglecting the escapes of volatile components.

As we can suppose certain losses of isocaprylic acid and glycerol from the reaction mixture, the total mass balance of components corresponding to the stage of process $n = 1$ (when the first sample is taken away from the batch at the same time) is expressed by

$$W_0 = W_1 + W_{I,1} + W_{G,1} + W_{W,1} \quad , \tag{1}$$

where

$$W_{I,1} = (A_0 - 1{,}7825 \times 10^{-5}\, n_{s,1}\, W_1)\, M_I \tag{2}$$

$$W_{G,1} = (B_0 - B_1) M_G / 3 \tag{3}$$

$$B_1 = 1{,}7825 \times 10^{-5}\, W_1 (n_{s,1} - n_{a,1} + n_{h,1}) \tag{4}$$

$$W_{W,1} = W_{WE,1} - W_1 w_{W,1} \tag{5}$$

$$W_{WE,1} = W_{W,0} + W_{We,1} \tag{6}$$

$$W_{We,1} = [1{,}7825 \times 10^{-5}\, W_1 (n_{s,1} - n_{a,1}) - C_0] M_W \tag{7}$$

Equations (1)–(7) apply if the following assumptions are fulfilled: The amounts of water created by reactions other than esterification are negligible; the amounts of other losses from reaction mixture than the losses of water, isocaprylic acid and glycerol are negligible as well, and other types of reactions of functional groups than esterification do not occur. Symbols in eqs. (1)–(7) designate the following: W_0 is the mass of the original mixture (before reaction), $W_0 = 898.31$ g, W_1 is the mass of the batch (the liquid reaction mixture) in the flask at the 1st stage of the process, $W_{I,1}$ is the mass of isocaprylic acid lost from the batch at the 1st stage of the process, $W_{G,1}$ is the mass of glycerol lost from the batch at the 1st stage of the process, $W_{W,1}$ is the mass of water lost from the batch at the 1st stage of the process, $W_{W,0}$ is the mass of water in the original mixture, $w_{W,0} = 3.117$ g, $W_{WE,1}$ is the mass of water created by esterification at the 1st stage of the process, $w_{W,1}$ is the mass function of water in the batch at the 1st stage of the process, M_I is the molecular weight of isocaprylic acid, $M_I = 144.2$, M_G is the molecular weight of glycerol, $M_G = 92.1$, M_W is the molecular weight of water, $M_W = 18$, $n_{a,1}$ resp. $n_{h,1}$ and $n_{s,1}$ is the acid number, resp. the hydroxyl number and the saponification number, at the 1st stage of the process, A_0 is the number of moles of carboxyl groups and two fold number of moles of anhydride groups in the original mixture, $A_0 = 6.244$, B_0 is the number of hydroxyyl groups in the original mixture, $B_0 = 7.226$, C_0 is the number of moles of anhydride groups in the original mixture, $C_0 = 1.813$, and B_1 is the number of moles of ester groups and hydroxyl groups in the batch at the 1st stage of the process.

Substituting from eqs. (2)–(7) into eq. (1), mass W_1 of the batch of the 1st stage of the process is calculated. Then the following masses are calculated by means of eqs. (2)–(7): masses of losses of isocaprylic acid and glycerol, mass of water created by esterification, and mass of water loss from the batch.

At further stages of the process ($n = 2, 3, \cdots$) it is necessary to take account of amounts of the samples previously taken away from the batch. The total mass balance of components at the nth stage of the process (when the nth sample is taken away from the batch) is given by

$$W_0 = W_n + \sum^{n-1} \overline{W}_i + W_{I,n} + W_{G,n} + W_{W,n} \tag{8}$$

where

$$W_{I,n} = (A_0 - 1{,}7825 \times 10^{-5} W_n - \sum^{n-1} a_i) M_I \tag{9}$$

$$a_i = 1{,}7825 \times 10^{-5} \overline{W}_i n_{s,i} \tag{10}$$

$$W_{G,n} = (B_0 - B_n - \sum^{n-1} b_i) M_G/3 \tag{11}$$

$$B_n = 1{,}7825 \times 10^{-5} W_n(n_{s,n} - n_{a,n} + n_{h,n}) \tag{12}$$

$$b_i = 1{,}7825 \times 10^{-5} \overline{W}_i (n_{s,i} - n_{a,i} + n_{h,i}) \tag{13}$$

$$W_{W,n} = W_{WE,n} - W_n w_{W,n} - \sum^{n-1} \overline{W}_i w_{W,i} \tag{14}$$

$$W_{WE,n} = W_{W,0} + W_{We,n} + \sum^{n-1} \overline{W}_{We,i} \tag{15}$$

$$W_{We,n} = [1{,}7825 \times 10^{-5} W_n(n_{s,n} - n_{a,n}) - C_{n-1}]M_W \tag{16}$$

$$C(n=2)_{n-1} = C_0 - (C_0 \overline{W}_1 / W_1) \tag{16a}$$

$$C(n=3)_{n-1} - [C(n=2)_{n-1} \overline{W}_{n-1} / W_{n-1}]$$

$$\cdots \tag{16b}$$

$$C(n=10)_{n-1} = C(n=9)_{n-1} - [C(n=9)_{n-1} \overline{W}_{n-1} / W_{n-1}] \tag{16i}$$

$$\overline{W}_{We,i} = \overline{W}_i W_{We,i} / W_i \tag{17}$$

Symbols in eqs. (8)–(17) designate the following: W_n is the mass of the batch in the flask at the nth stage of the process, W_i is the mass of the batch in the flask at the $i$thstage of the process, $\overline{W}_i$ is the mass of the sample taken away from the batch at the ith stage of the process, $W_{W,n}$ is the total loss of water from the batch at the nth stage of the process, $n_{a,n}$, resp. $n_{h,n}$ and $n_{s,n}$, is the acid number, resp. the hydroxyl number and the saponification number, at the nth stage of the process, and $w_{W,n}$ is the mass fraction of water in alkyd resin at the nth stage of the process.

Substituting from eqs. (9)–(17) into eq. (8), the mass W_n of the batch at the nth stage of the process is calculated. Then the following masses are calculated: the masses of losses of isocaprylic acid and glycerol [by means of eqs. (9)–(13)], the mass of water created by esterification [by means of eqs. (15)–(17)], and the mass of total loss of water from the batch [by means of eq. (14)].

If no sample is taken away from the batch at each stage of the process, the mass $W(\mathrm{O})_n$ of the batch at the nth stage of the process is given by eq. (18), the mass $W(\mathrm{O})_{WE,n}$ of water created by esterification at the nth stage of the process is given by eq. (20), and the mass $W(\mathrm{O})_{W,n}$ of the total loss of water from the batch at the nth stage of the process is given by eq. (21). Conversion of functional groups in the reaction mixture at the nth stage of the process equals that achieved in the nth sample itself when the samples were taken away from the batch:

$$W(\mathrm{O})_n = \frac{W_n(W(\mathrm{O})_{n-1} - W_{I,n} + W_{I,N-1} - W_{G,n} + W_{G,n-1})}{W_{n-1} - \overline{W}_{n-1} - W_{I,n} + W_{I,N-1} - W_{G,n} + W_{G,n-1}} \tag{18}$$

$$W(\mathrm{O})_{We,n} = W(\mathrm{O})_n W_{We,n}/W_n \tag{19}$$

$$W(\mathrm{O})_{WE,n} = W_{W,0} + W(\mathrm{O})_{We,n} \tag{20}$$

$$W(\mathrm{O})_{W,n} = W(\mathrm{O})_{WE,n} - w_{W,n}W(\mathrm{O})_n \tag{21}$$

Equations (181)–(21a) apply for $n=2$:

$$W(\mathrm{O})_2 = \frac{W_2(W_1 - W_{I,2} + W_{I,1} - W_{G,2} + W_{G,1}}{W_1 - \overline{W}_1 - W_{I,2} + W_{I,1} - W_{G,2} + W_{G,1}} \tag{18a}$$

$$W(\mathrm{O})_{We,2} = W(\mathrm{O})_2 W_{We,2}/W_2 \tag{19a}$$

$$W(\mathrm{O})_{WE,2} = W_{W,0} + W(\mathrm{O})_{We,2} \tag{19b}$$

$$W(\mathrm{O})_{WE,2} = W_{W,0} + W(\mathrm{O})_{We,2} \tag{20a}$$

$$W(\mathrm{O})_{W,2} = W(\mathrm{O})_{WE,2} - w_{W,2}W(\mathrm{O})_2 \tag{21a}$$

EXPERIMENTAL

Preparation of Alkyd Resin

The following materials were used for alkyd synthesis: isocaprylic acid (BASF), phthalic anhydride, glycerol, and pentaerythritol. The last three materials are inland products. Results of analyses of the materials are given in Table I. A reaction glass flask of 1.5 L with three necks was used for preparation of the alkyd resin. The flask, heated by electrical mantle, was provided with two thermometers (for indicating and controlling temperature) a stirrer and a back column (its inner diameter was 4.5 cm, its length was 22 cm, and it was packed by Raschig's rings of diameters 0.6–0.8 mm). A water-cooled condenser was joined to the apparatus beyond the column.

All original reactants in the flask were heated in inert atmosphere of nitrogen. When the temperature of 172°C was achieved, water of reaction

TABLE I
Results of Analyses of Materials[a]

Material	n_a (mg KOH/g)	n_h (mg KOH/g)	$w_W \times 10^2$
Isocaprylic acid	378.10	—	0.50
Phthalic anhydride[b]	755.52	—	—
	384.97	—	—
Glycerol	—	1788	1.43
Pentaerythritol	—	1580	0.04

[a] n_a is the acid number, n_h is the hydroxyl number, and w_W is the mass fraction of water.
[b] 755.52 is the acid number determined by analysis in aqueous medium, 384.97 is the acid number determined by analysis in nonaqueous medium; the material consists of phthalic anhydride (97.84 mass %) and phthalic acid (2.13 mass %).

began to destill off. Then the temperature of the batch was gradually increased, and the samples were taken away from the batch at certain time intervals. The amounts of condensed water were measured. In a period of 3 h six samples were taken away, and the temperature of the batch was increased to 220°C. This temperature was kept until the end of the synthesis. The total number of samples taken away was 10.

Analysis of Alkyd Resin

Determination of Acid Number

Two grams of the sample were dissolved in 25 mL of mixed solvent (2 volumes of benzene and 1 volume of ethyl alcohol) at room temperature. The solution was titrated with 0.1*N* alcoholic KOH to a phenolphthalein end point.

Determination of Hydroxyl Number

Two grams of the sample were dissolved in 5 mL of pyridine and treated with 5 mL of the mixture of 25 vol % acetic anhydride in toluene at boiling temperature for 1 h. The cooled solution was titrated with 0.5*N* alcoholic KOH to a phenolphthalein end point.

Determination of Saponification Number

One-half gram of the sample was treated with 25 mL of 0.5*N* alcoholic KOH at boiling temperature. An excess of KOH was titrated with 0.5*N* HCl to a phenolphthalein end point.

Determination of Water

The content of water in resin was determined by titrometric method using Karl Fischer reagent (mixture of pyridine, sulfur dioxide, methanol, and iodine). Approximately 20 mL of pyridine was placed into titration flask, and traces of moisture were titrated by using Karl Fischer reagent (electrometric titration by the dead-stop end point method using two polarized platinum electrodes). Then a weighted sample was added into the flask, and

after its dissolution the solution was again titrated to the dead-stop end point.

RESULTS

Composition of the original (before reaction) mixture of materials is shown in Table II. Analytical values of the samples withdrawn from the batch during alkyd synthesis are given in Table III. Masses of total losses of isocaprylic acid ($W_{I,n}$) and glycerol ($W_{G,n}$) from the batch, the mass of water created by esterification ($W_{WE,n}$), and the mass of total loss of water from the reaction mixtrue ($W_{W,n}$) up to nth stage of the process are given in Table IV.

The nth stage of the process is characterised by the nth degree of conversion p_n of the reaction mixture resting in the reaction flask. p_n is given by

$$p_n = \frac{n_{s,n} - n_{a,n}}{n_{s,n}} \tag{22}$$

A mean degree of conversion $\bar{p}_n$ of reaction mixture resting in the reaction flask at the nth stage of the process and samples previously withdrawn is given by eq. (23). The value of $\bar{p}_n$ is lower than the value of p_n.

$$\bar{p}_n = \frac{W_n (n_{s,n} - n_{a,n}) + \sum_{}^{n-1} \bar{W}_i (n_{s,i} - n_{a,i})}{W_n n_{s,n} + \sum_{}^{n-1} \bar{W}_i n_{s,i}} \tag{23}$$

Dependences of the masses of the above-mentioned components on the mean degree of conversion $\bar{p}$ are shown in Figure 1.

If no samples at all were withdrawn from the batch up to the nth stage

TABLE II
Composition of Original Mixture[a]

m	Material	$W_{0,m}$ (g)	$B_{0,m}$	$A_{0,m}$	$W_{W,0,m}$ (g)
1	Isocaprylic acid	378.06	—	2.548	1.890
2	Phthalic anhydride[b]	274.39	—	3.696	—
3	Glycerol	81.22	2.589	—	1.161
4	Pentaerythritol	164.64	4.637	—	0.066
Total mass W_0 (g)		898.31	—	—	—
Total number of moles A_0 and B_0		—	7.226	6.244	—
Total mass of water $W_{W,0}$ (g)		—	—	—	3.117

[a] $W_{0,m}$ is the mass of mth material, $A_{0,m}$ is the number of moles of carboxylic groups in the 1st material, resp. the number of moles of carboxylic groups and twofold number of moles of anhydride groups in the 2nd material, $B_{0,m}$ is the number of moles of hydroxyl groups in the mth material, and $W_{W,0,m}$ is the mass of water in mth material.

[b] The second material consists of 268.46 g of phthalic anhydride and 5.84 g of phthalic acid; the number of moles of phthalic anhydride (C_0) is 1.813, number of moles of phthalic acid is 0.035.

TABLE III
Synthesis of Alkyd Resin—Analytical Values[a]

n	$\overline{W}_n$ (g)	$V_{W,n}$ (mL)	$V_{W,n}$ / $V_{W,n-1}$	$w_{W,n}$ × 10^2	$n_{s,n}$ (mg KOH/g)	$n_{a,n}$ (mg KOH/g)	$n_{h,n}$ (mg KOH/g)
1	28.1	10	10	0.86	402.3	211.5	275.5
2	37.7	20	10	0.75	405.9	181.1	238.6
3	22.0	30	10	0.53	412.4	152.7	213.9
4	31.5	40	10	0.28	417.7	118.5	181.0
5	23.1	50	10	0.16	425.1	86.2	149.4
6	29.5	60	10	0.08	430.3	44.7	110.3
7	38.2	62	2	0.07	432.2	31.7	94.9
8	41.1	64.5	2.5	0.08	432.5	29.5	96.0
9	39.2	—	—	0.05	432.6	18.1	85.3
10	—	—	—	0.07	432.5	16.4	81.3

[a] $\overline{W}_n$ is the mass of nth withdrawn sample at nth stage of the process, $V_{W,n}$ is the volume of the total loss of water (water condensed in the water-cooled condenser) from reaction mixture up to nth stage of the process, $w_{W,n}$ is the mass portion of water in the batch in reaction flask at the nth stage of the process (it equals the mass portion of water in nth withdrawn sample), $n_{s,n}$, resp. $n_{a,n}$ and $n_{h,n}$, is the saponification number, resp. the acid number and the hydroxyl number, of the mixture in reaction flask at nth stage of the process (these numbers equal to the respective ones of nth withdrawn sample).

of the process, degree of conversion p_n at the nth stage of the process would equal that reached in the reaction mixture resting in the reaction flask when the nth sample was withdrawn [see eq. (22)].

Masses $W(O)_{WE,n}$, $W(O)_{W,n}$, $w_{W,n}W(O)_n$ (mass of water in the batch at nth stage of the process) and degree of conversion p_n are given Table V.

Dependences of the masses of above mentioned components on degree of conversion p are shown in Figure 2.

DISCUSSION

It was found out that isocaprylic acid and glycerol escaped partly from the liquid reaction mixture. It is evident that changes of the losses of these compounds are not regular during alkyd synthesis. Mean values of the losses

TABLE IV
Synthesis of the Alkyd Values Calculated by Means of Eqs. (1)–(17) When Samples Are Withdrawn from the Batch

n	$\overline{p}_n$	$W_{I,n}$ (g)	$W_{G,n}$ (g)	$W_{WE,n}$ (g)	$W_{W,n}$ (g)	$W_{W,n}$ 1 $W_{W,n-1}$ (g)
1	0.464	47.6	13.2	19.9	12.8	12.8
2	0.551	27.9	9.7	30.5	24.2	11.4
3	0.620	45.2	12.8	36.7	32.3	8.1
4	0.698	41.9	11.8	45.3	42.6	10.3
5	0.766	57.0	15.6	51.2	49.4	6.8
6	0.848	53.4	14.2	60.1	58.9	9.5
7	0.872	49.7	14.2	63.1	61.9	3.0
8	0.875	54.2	14.3	63.0	61.7	−0.2
9	0.894	46.6	12.2	65.7	64.6	2.9
10	0.896	42.7	11.9	66.5	65.3	0.7

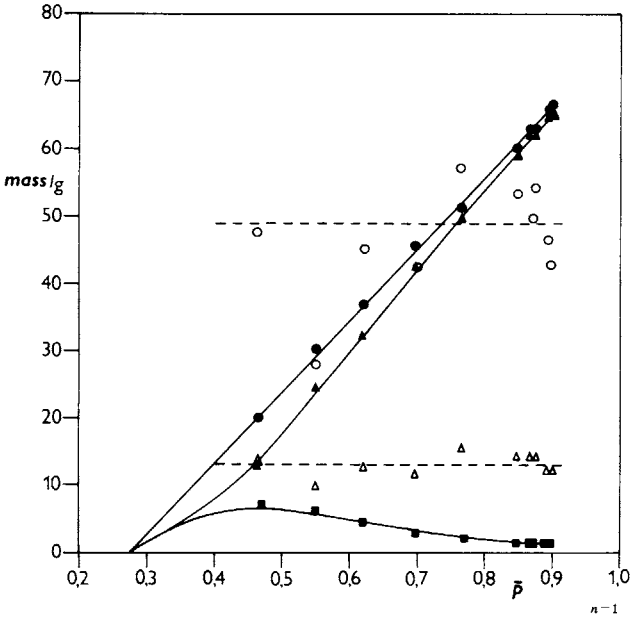

Fig. 1. Dependences: (●) $W_{WE,n} - \bar{p}_n$; (▲) $W_{W,n} - \bar{p}_n$; (■) $(w_{W,n}W_n + \sum_{1}^{n-1} w_{W,i}\overline{W}_i) - \bar{p}_n$, (○) $W_{L,n} - \bar{p}_n$; (△) $W_{G,n} - \bar{p}_n$.

are 49 g of isocaprylic acid and 13 g of glycerol. Deviations of losses at different stages of the process from the mean values are small for glycerol and something greater for isocaprylic acid. Our arrangement of alkyd preparation process caused that roughly constant (unchanging) amounts of is-

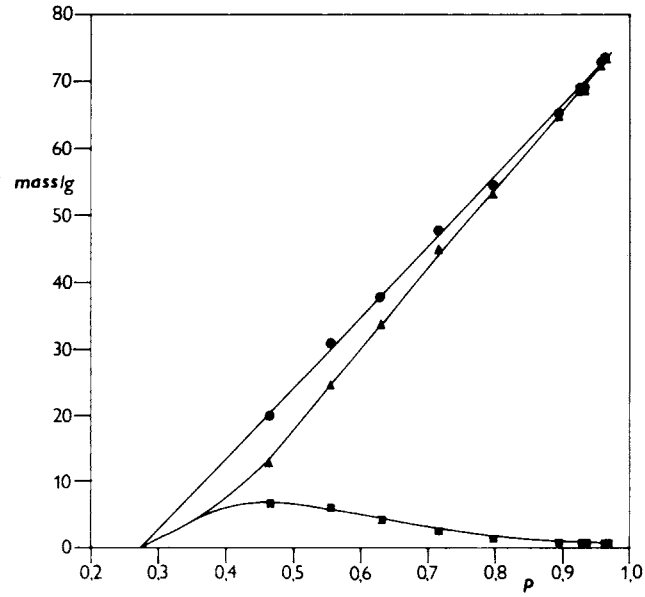

Fig. 2. Dependences: (●) $W(O)_{WE,n} - p_n$ (▲) $W(O)_{W,n} - p_n$ (■) $w_{W,n}W(O)_n - p_n$.

ocaprylic acid and glycerol are present in the flask space above liquid batch and in the back column in the range of $p = 0.46–0.96$.

As it is evident from Tables III and IV, the measured losses of water from reaction mixture (water condensed in a water-cooled condenser) are in a good agreement with calculated values of losses of water from reaction mixture.

No esterification water is practically created up to degree of conversion $p = 0.277$ as only anhydride groups react with hydroxyl groups at the beginning of reaction. As we can see from Figure 1, the total loss of water from reaction mixture increases more quickly than linearly at the range of $p = 0.277–0.5$, then it increases linearly and most quickly, and the increase of the total water loss is again a little slower in the range of $p = 0.75–0.96$.

It corresponds with the course of dependence of the water content in the reaction mixture on degree of conversion. The content of water in reaction mixture increases quickly from 0 g up to 7 g in the range of $p = 0.277–0.5$; then it decreases practically linearly as conversion preceeds (the range of $p = 0.5–0.75$), and the decrease of the water content in reaction mixture is very slow at the range of $p = 0.75–0.96$. If no samples were withdrawn from the reaction mixture during alkyd synthesis, the content of water in reaction mixture would be 0.5 g at $p = 0.96$.

As we can see in Figure 3, at first the water content in reaction mixtue decreases quickly as $\overline{M}_n$ increases from 250 up to 400, then it decreases more slowly (the range of $\overline{M}_n = 400–800$), and the decrease of the water content in reaction mixture is very slow above $\overline{M}_n = 800$. The water content in the reaction mixture is 0.05–0.07 mass % at $\overline{M}_n = 1400$. This value is very low and it is practically impossible to further remove water from reaction mixture without lowering pressure above it.

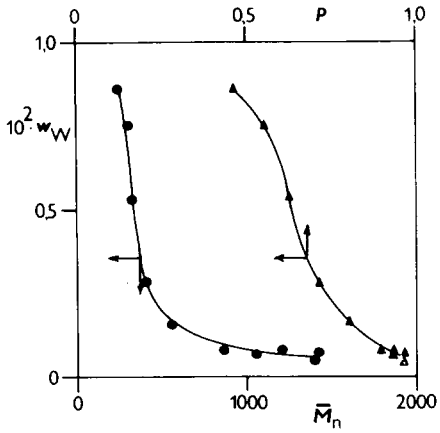

Fig. 3. Dependence of percentual content of water in reaction mixture on number-average molecular weight $\overline{M}_n$ (●) resp. degree of conversion p (▲).

CONCLUSION

The presented way of treatment of analytical values provided by analyses of the samples withdrawn from the batch in the course of preparation of alkyd polyester makes it possible to determine the losses of volatile reactants from reaction mixture. In our case it was found out that mean percentual values of losses are 13 mass % of isocaprylic acid and 16 mass % of glycerol form the original batch. It is necessary to realize that if the compounds occurring in the space above liquid reaction mixture are not removed (by lowering pressure) at the end of synthesis, they will go into cooled reaction mixture and the degree of conversion finally reached will be depressed.

It was found out that losses of water from reaction mixture do not increase steadily. Calculation of amounts of water losses from reaction mixture enables to control the course of alkyd synthesis mostly by measuring the amount of condensed water.

The presented treatment of results also provides the values necessary for physical evaluation of alkyd resin that will be presented in the second part of our paper.

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