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INFLUENCE OF POLYESTERURETHANE PLASTICIZER ON THE KINETICS OF POLY(VINYL CHLORIDE) DECOMPOSITION PROCESS

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Poly(vinyl chloride) (PVC), plasticized by di(2-ethylhexyl) phthalate (DEHP), medium molecular mass polyesterurethane (PU) or by both plasticizers, was thermally degraded under dynamic thermogravimetric conditions and the kinetics of decomposition was studied by isoconversional methods and by non-linear regression. It has been found that the initial decomposition temperature is higher for PVC plasticized with PU, as compared with PVC plasticized with di(2-ethylhexyl) phthalate (DEHP) or plasticized with PU/DEHP, and thermal degradation shows features of a multi-step complex process. Application of polymeric plasticizer leads to the increase and a 'smoothing' effect in the course of energy of activation and pre-exponential factor at the initial stage of decomposition indicating thus the hindered migration of medium molecular mass compound from PVC matrix (in comparison with PVC containing monomeric DEHP) due to steric hindrances as well as due to specific interactions between C=O and Cl groups along the macrochains. Kinetic model function of the decomposition process of PVC/DEHP and PVC/DEHP/PU blends was found to be a two-stage autocatalyzed reaction of n^{th} order; autocatalytic effect is associated most likely with the role of HCl formed during PVC decomposition. For PVC/PU blend best fit was found by non-linear regression for a two-stage scheme in which first stage was Prout–Tompkins model and the second was autocatalytical model of n^{th} order – the first one involves particle disintegration, which was promoted by product generation at branching PVC 'pseudo-crystals' nuclei, thus exposing more surface on which decomposition reaction proceeds.

Keywords: *kinetics of degradation, polymeric plasticizer, PVC, TG*

Introduction

Migration of phthalate plasticizers from poly(vinyl chloride) (PVC) is an important phenomena from both fundamental and application point of view. The toxicity of phthalate esters, particularly di(2-ethylhexyl) phthalate (DEHP), has been a matter of serious concern [1–3] as they have been found to migrate from PVC-based medical and childcare articles, especially those which are known to be mouthed.

The use of low-migration polymeric plasticizers can be considered as a good alternative to common monomeric plasticizers, e.g. phthalates or adipates.

In industrial practice, the PVC-based blends are mixtures of PVC with miscible or non-miscible polymers, usually containing liquid (monomeric) plasticizers that can be handled easily in conventional PVC equipment. PVC blends with miscible or non-miscible polymers alone play an important and growing role but processing is more difficult [4]. Some examples of flexible polymeric plasticizers include acrylonitrile/butadiene rubber, copolymers of ethylene/acrylic monomer, ethylene/vinyl acetate and styrene/acrylonitrile [5–7]. Polymeric propyleneglycol adipate has also been applied for preparation of PVC plastisols in a Brabender mixer [8]. The thermal stability and kinetics of decomposition were then studied by TG method showing that compositions with macromolecular plasticizer were less thermally stable compared to traditional plastisols. However, during preparation of the latter, thermal stabilizers, such as metal stearates or phenolic compounds, were added.

Also kinetic analysis of the evaporation of poly(1,3-butylene adipate) that was used as polymeric plasticizer for PVC has been performed [9]. The process of plasticizer loss from PVC matrix followed the kinetic laws of the first-order reaction. The kinetic dependencies showed that for the investigated system the process of migration of polymeric plasticizer from the surface is the rate-determining process, which energy of activation was in the 42–81 kJ mol^{-1} range.

Świerz-Motysia *et al*. have investigated the performance of semi-solid polyesterurethanes (PU) as plasticizers for PVC – the obtained compositions had homogeneous one-phase structure, as evidenced by SEM and DMTA techniques, and were displaying very good aging stability and resistance to extraction into hydrocarbons and oils [10–12]. Pursuing further the investigations on this subject, the current work aims at kinetic description of the thermal degradation of these novel PVC/PU blends as compared with traditional DEHP-containing PVC plastisols.

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Experimental

Materials

Suspension PVC (K-70) was product of ANWIL SA, Włocławek, Poland. Its molecular mass was determined by GPC technique (Shimadzu CR4A Chromatopac using PL gel Mixed-C columns) as M_n=52000 and M_w=140000.

Monomeric plasticizer – di(2-ethylhexyl) phthalate – was produced by Boryszew SA, Sochaczew, Poland.

Polyesterurethane (PU) with M_w=13000 was synthesized at ICRI by prepolymer method using isophorone diisocyanate and a copolymer of 1,6-hexanediol and adipic/phthalic acid (Bester 195 from Poliolchimica S.P.A.). Cycloaliphatic isophorone diisocyanate was applied to obtain polyurethanes with possibly high resistance to the thermal degradation caused by free-radical processes.

The detailed description of the preparation procedure of the PVC systems was presented elsewhere [11]. Description of the samples is given in Table 1.

Table 1 Description of the samples

Sample	Plasticizer/mass%
1	DEHP (33.5)
2	DEHP (18.5)/PU (15)
3	PU (50)

Technique

Thermogravimetric analysis was performed on a Netzsch TG 209 thermal analyser, operating in a dynamic mode at a heating rate of 2.5, 5, 10 and 20 K min^{-1}. The conditions were: sample mass ~7 mg, atmosphere argon, open α-Al_2O_3 pan. The raw data were converted to ASCII files and kinetic analysis was carried out using an in-house program and a Netzsch Thermokinetic Program (v. 99/10) in the calculation procedure, the corresponding kinetic parameters are computed by nonlinear regression which is the iterative calculation of the minimum sum of least squares, LSQ. For the solution of the system of differential equations, a 5th-degree Runge–Kutta method (Prince–Dormand algorithm) is employed as a subprogram. This subprogram is, for its part, tied into a hybrid regularized Gauss–Newton method.

Results and discussion

Initially, TG analysis was performed at 10 K min^{-1} to ascertain the thermal stability of the samples (Fig. 1).

It can be seen that the initial decompostion temperature of sample 3 is the highest, reaching 252°C, whereby for samples 1 and 2 it is 215 and 225°C, respectively. Degradation shows features of a multistep complex process to obtain additional information of the nature of this process kinetic analysis was performed by isoconversional methods that yield values of activation energy (E_a) and pre-exponential factor (A) [13–18].

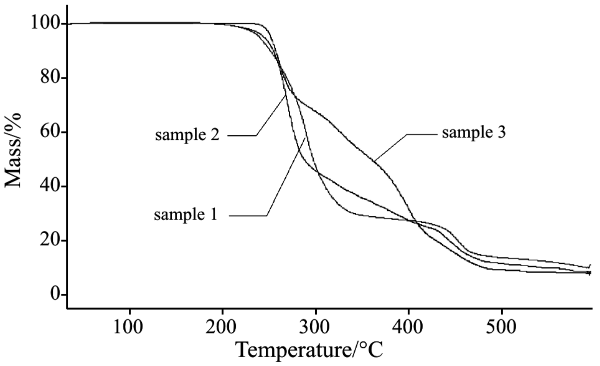

Fig. 1 TG profiles of samples 1–3 at 10 K min^{-1} under argon atmosphere

Ozawa–Flynn–Wall analysis of the thermal degradation of sample 1, depicted in Fig. 2, indicate that there are three regions of energy of activation and pre-exponential factor changeability (Fig. 3) which arise from migration of the monomeric plasticizer and decomposition of PVC matrix.

The first region is most likely associated with migration of plasticizer which is lost first from the surface and then from the bulk. As a matter of fact, investigations of the migration of DEHP in PVC under heating by depth analysis using FTIR spectroscopy lead to the conclusion that depth profiles depend on the stabilizers used; for PVC/DEHP stabilized with di-*n*-butyl-tin-dilaurate, DEHP seems to be lost first from the surface, and then diffuses from the polymer matrix to the surface, which is a typical pattern of diffusion control [19]. Additionally, in PVC/DEHP containing di-*n*-butyl-tin-dilaurate and di-*n*-butyl-tin-maleate polymer DEHP evolution was less intensive and characterized by a smaller rate coefficient – this is

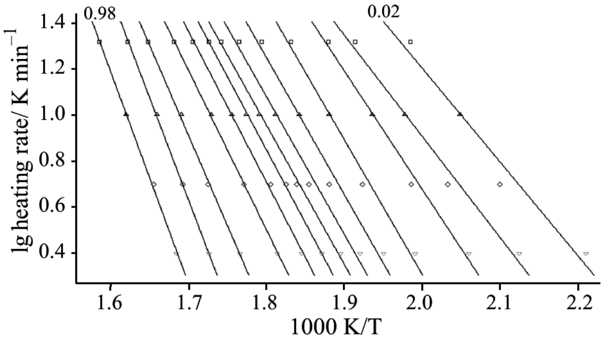

Fig. 2 Ozawa–Flynn–Wall analysis of the thermal degradation of sample 1 at 2.5, 5, 10 and 20 K min^{-1} under argon atmosphere

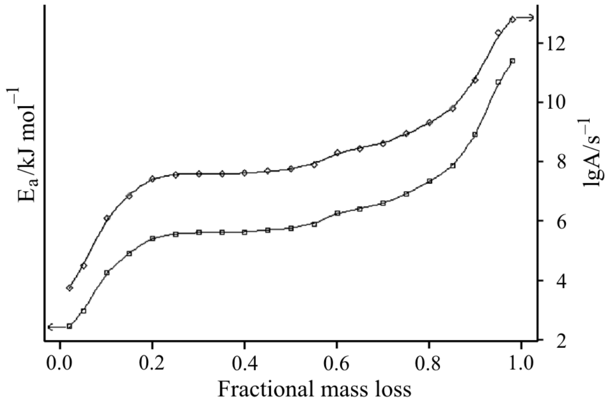

Fig. 3 Activation energy (E_a) and pre-exponential factor (A) *vs*. degree of conversion for the degradation process of sample 1 calculated by Ozawa–Flynn–Wall method

a typical surface control pattern. Isothermal mass loss kinetics of plasticized PVC at the temperature range 85–120°C showed that at this temperature range the plasticizer loss was the only significant source of mass change, but still at least two different kinetic regimes were involved, as evidenced by the characteristic shape of Arrhenius plot [20]. It could be supposed that an almost continuous plasticizer monolayer exists at the sample surface, making the evaporation rate practically insensitive to the plasticizer bulk concentration. Indeed, when this latter decreases, the free volume fraction and, thus, the plasticizer diffusivity decreases and can reach a critical value beyond which the whole process becomes diffusion-controlled. A simple kinetic model cannot, therefore, describe the whole plasticizer-loss process since there is probably a kinetic transition stage between the two regimes. For PVC plasticized by DEHP it has been observed that a progressive increase of plasticizer amount lead to more thermally stable mixtures. It would indicate that the resin degradation starts before the plasticizer decomposition takes place [21]. This behaviour was confirmed in a broader range of plasticizer concentrations and using PVC plastisols of different formulation [22, 23]. It was assumed that when thermal degradation starts the only associated process is plasticizer evaporation and it determines the reaction rate. During evaporation free holes in the plastisol structure are formed which can be considered as initiation (or active) centers of the dehydrochlorination process, as postulated earlier [24]. Dehydrochlorination once started shows an autocatalytic effect that overwhelms other kinetic paths.

At higher temperature a gradual decomposition of the PVC matrix takes place by splitting off hydrogen chloride; during HCl loss polyene sequences are formed that are active in secondary reactions leading to cross-linking and formation of aromatic pyrolysates [25–27].

Non-linear regression was then applied for determination of the $f(\alpha)$ kinetic model function, the best fit (based on F-test) was found for a two-stage autocatalyzed reaction of n^{th} order.

Autocatalytic effect is associated most likely with the role of HCl formed during PVC decomposition – the first step is the formation of a double bond randomly along the polymer chain via a free radical or a 1,2-unimolecular elimination of HCl. The second and third steps constitute the chain elimination. Bacaloglu and Fisch proposed that in the second step a HCl molecule is eliminated from a *cis*-γ-alkyl-allyl chlorine through a six-center transition state generating a conjugated diene or polyene [28]. Next is a HCl-(auto) catalysed proton rearrangement generating a new *cis*-γ-alkyl-allyl chlorine from the conjugated polyene.

For sample 2, kinetic analysis by Friedman method (Fig. 4) leads to conclusion that the presence of PU as polymeric plasticizer causes an increase and ‘smoothing’ of the energy of activation and pre-exponential factor *vs*. degree of conversion profile (up to $\alpha<0.7$) (Fig. 5).

Kinetic model function was the same as in the case of sample 1 evidencing that partial replacement of DEHP by PU does not change the mechanism of PVC plastisol decomposition.

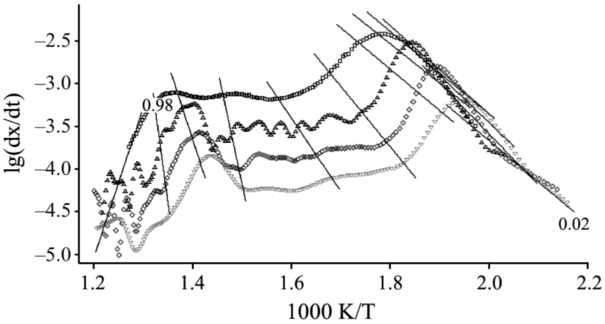

Fig. 4 Friedman analysis of the thermal degradation of sample 2 at 2.5, 5, 10 and 20 K min^{-1} under argon atmosphere

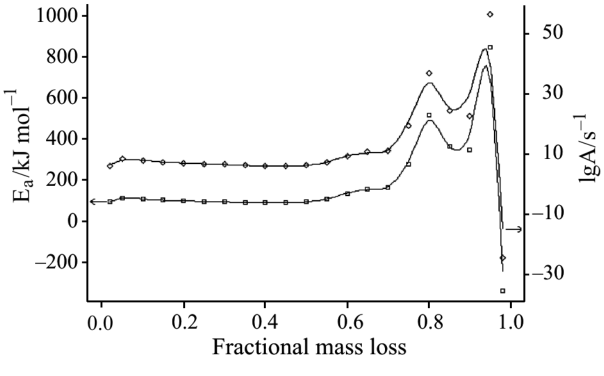

Fig. 5 Activation energy (E_a) and pre-exponential factor (A) *vs*. degree of conversion for the degradation process of sample 2 calculated by Friedman method

It could be expected that the activation energy would be higher as the molecule of plasticizer is larger and degree of branching greater. The motion of branched molecules is realized through cooperative segmental motions, similar to macromolecular coil. For polymeric plasticizer its crystallinity determines mobility of amorphous phase; additionally, polarity of matrix and plasticizer is also a factor contributing to the complex behaviour of the system.

It is noteworthy that the physical meaning of the activation energy, as described by Moisan who investigated diffusion process of stabilizers and antioxidants from PE, is such that one part of activation energy is attributed to the deformation of polymer matrix and the other to the deformation of the molecules of diffusant [29]. Microstructure of PVC plasticized with DEHP was studied by combination of ^{13}C solution NMR and ^{13}C solid-state NMR (CP/MAS and MAS); two distinct (micro)phases with considerably different chain mobilities (at least at elevated temperature) have been detected – the NMR relaxation behaviour of the two fractions was typical of partially crystalline polymers [30]. No experimental results indicated a (significant) fraction of a possible third phase of intermediate mobility which could be assigned to the amorphous phase. As a consequence, PVC could be regarded as a two-phase system consisting of a rigid and a mobile PVC phase. The rigid fraction was thereby assumed to be completely due to crystallized chain units whereas the mobile fraction was assigned to the amorphous phase. In a 1:1 (mass/mass) PVC/DEHP system, DEHP was homogeneously located only in the amorphous phase of PVC [31]; it could be assumed that DEHP acts as a type of solvent for this phase. Special attention was paid to the dynamics of PVC-DEHP interactions by ^{13}C CP/MAS NMR spectroscopy – it has been observed that the chemical shift of =CH–Cl group of PVC moves downfield as the concentration of DEHP is increased [32]. This effect was attributed to the hydrogen bonding between Cl–CH···O=C=, and generally, conformation of PVC changes due to the hydrogen bonding interactions between PVC and DEHP, where DEHP solvated the PVC. By presenting the dimensionless value T_2/T_2° (T_2 – the spin-spin relaxation time of the plasticizer inside the polymer, T_2° – the spin-spin relaxation time of pure plasticizer) *vs*. DEHP concentration it was possible to select two ranges of plasticization – in the first one up to 20 mass/mass% of DEHP in PVC the mobility of plasticizer molecules quickly decreases compared with that of pure DEHP, indicating strong interactions of the plasticizer with the macromolecules. The plasticizer molecules cannot penetrate any further into the spaces between molecules. Above the given threshold concentration, the mobility of plasticizer molecules rapidly increases causing effective plasticization of PVC. Any attempt to increase the DEHP concentration above 50% will progressively lead to phase separation. The first stage is called intraspherulitic or molecular plasticization, whereby the second range indicated interspherulitic or structural plasticization [33]. The complex plasticization behaviour of PVC was proven previously by Geil *et al*. using replicas of freeze-fractured surfaces of plasticized polymer [34]. Such samples revealed a nodular microstructure on three levels of scale: 100 to 500 Å, 0.1–0.5 μm, and 1 to 10 μm. The smallest nodules were found to increase in size with the addition of the plasticizer. This behaviour was confirmed using SAXS and is thought to be caused by the plasticizer preferentially diffusing into the smallest nodular structures.

PVC/PU blend (sample 3) thermal decomposition is characterized by relatively stable *E* and *A* profile, apart from the final stage for $\alpha>0.8$ (Fig. 6).

Best fit was found by non-linear regression for a two-stage scheme in which first stage was Prout–Tompkins model and the second was autocatalytical model of n^{th} order (Fig. 7).

The Prout–Tompkins equation shows also the dependence of the rate on both the amount of reactant left and the amount of product formed, known as auto-

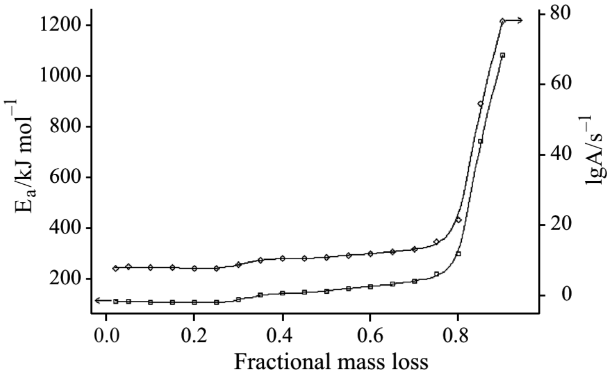

Fig. 6 Activation energy (E_a) and pre-exponential factor (A) *vs*. degree of conversion for the degradation process of sample 3 calculated by Ozawa–Flynn–Wall method

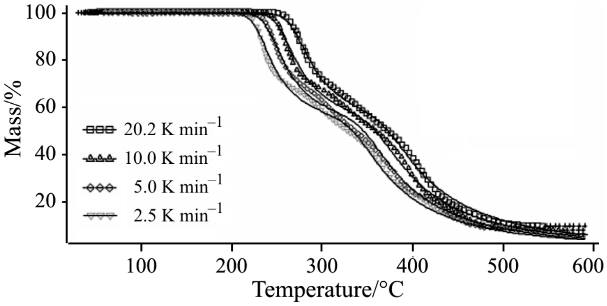

Fig. 7 Comparison of the experimental data (geometrical symbols) with modelled values (solid lines) for the thermal decomposition of sample 3

catalysis. It is noteworthy that the mechanistic model on which the Prout–Tompkins model was originally formulated was based on the concept of 'nucleus branching', analogous to homogeneous chain reactions. It involves particle disintegration, which was promoted by product generation at branching nuclei, thus exposing more surface on which reaction proceeds [35]. That may be associated with PVC structure composed of 'pseudo crystals' which differ widely in perfection and size, causing a wide melting range in which both reversible melting and reorganization to crystals with a higher stability occurs [36]. The average thickness of microcrystallites, primarily ordered perpendicular to the polymer backbone, is not well-known but estimates range between 7 and 15 Å [37]. They act as physical cross-links which contribute to the strength of PVC [38] which shows itself a kind of structural hierarchy – it is a powder of about 100–150 μm, called grains, consisting of skin and tight agglomerates (ca. 10 μm); the agglomerate is composed of primary particles (ca. 1 μm) which in turn consist of domains (ca. 0.1 μm); the domain is made up of microdomains (ca. 10 nm) which are held internally by the above mentioned microcrystallites [39].

On the other hand, in solution-cast films two crystal populations found have been denoted as A and B, respectively [40]. Type A crystals are hypothesized to represent folded-chain lamellar crystals formed by arrangement of syndiotactic sequences; they are the more perfect and hence have a slightly smaller *d*-spacings and lattice parameters. Crystals of type B are thought to correspond to fringed micelle crystals, formed by the bundling of adjacent chains with short stereoregular segments. The diffraction lines for type B crystals are broad, suggesting they are smaller and less perfect than type A crystals. Recently, the microdomain model of crystallinity in PVC has been verified through the use of HRTEM and image analysis techniques [41]. The small percentage of crystallinity, suggested as being present on the basis of thermal and X-ray techniques, has been shown to exist as ordered regions, but the exact nature of the biaxial orientations observed in the cast films produced here is not certain. It may indicate the presence of both fringed micelle and folded-chain crystals similar to those found in stretched PVC gels, with the folded-chain crystals significantly smaller than those found previously. More probably, the presence of biaxial strain during or after film formation has resulted in biaxially oriented fringed micellar type crystallites. Moreover, interpretation of WAXS patterns of PVC seems to confirm the existence of a certain small amount of a crystalline phase consisting of an orthorhombic cell formed by syndiotactic chains in the planar zig-zag configuration [42]. However, the crystalline percentages are higher than can be accounted for in terms of crystallization from syndiotactic sequences only. This is so-called 'crystallinity enigma' of PVC, as discussed by Hobson and Windle [43]. The inclusion of isotactic chains that can emulate the syndiotactic conformation in otherwise syndiotactic crystals has been proposed as an explanation for the higher than calculated crystallinities obtained for PVC. On the other hand, more and more attention is paid at non-crystalline phase where presence of interchain orientational correlations with highly parallel segments tending to occur in small localized clusters rather than being homogeneously distributed is assumed [44]. As it can be seen, the complete morphological and structural description of a PVC/PU blend is extremely complex since both PVC, with its hierarchical microstructural arrangement, and PU, containing alternate soft- and hard segment units, contribute to the multi-component blend system thus affecting considerably its thermal properties. Hence, the different kinetic behaviour of PVC plasticized with PU in comparison with PVC containing monomeric DEHP can be explained in terms of hindered migration of medium molecular mass compound from PVC matrix due to steric hindrances as well as due to specific interactions between C=O and Cl groups along the macrochains. It is well-known that chlorinated polymers are miscible with many polyesters and it has been shown that the miscibility of these blends can be due to hydrogen bonding between the C=O groups of the polyesterurethane and the α-hydrogen of chlorinated polymer [45, 46] or a dipole–dipole –C=O···Cl–C– interactions [47, 48]. By the appropriate arrangement of Cl atoms in the polymer structure, the latter interaction will become a factor in controlling the properties of the blend. This will occur as the greater the number of non-repulsive interactions which exist on a molecular level between the blend's components, the more dense will be the arrangement of the microstructure leading to an improvement of the system's physical properties. On the other hand, the rate of diffusion of volatile products through microphase domain structure may differ due to changes in morphology arrangement thus considerably affecting the overall decomposition route.

Conclusions

Application of a polymeric plasticizer – medium molecular mass polyesterurethane – leads to the increase and a 'smoothing' effect in the course of energy of activation and pre-exponential factor at the initial stage of PVC plastisols degradation indicating thus the hindered migration of medium molecular mass compound from PVC matrix (in comparison with PVC containing monomeric DEHP) due to steric hindrances as well as due to specific interactions between C=O and Cl groups along the macrochains. It has been also found that kinetic model function of the decomposition process of PVC/DEHP and PVC/DEHP/PU blends was a two-stage autocatalysed reaction of n^{th} order; autocatalytic effect is associated most likely with the role of HCl formed during PVC decomposition. For PVC/PU blend best fit was found by non-linear regression for a two-stage scheme in which first stage was Prout–Tompkins model and the second was autocatalytical model of n^{th} order – the first one involves particle disintegration, which was promoted by product generation at branching PVC 'pseudo-crystals' nuclei, thus exposing more surface on which decomposition reaction proceeds.

Generally, hindered migration of a plasticizer is an extremely important parameter in medical applications, so the obtained results may be applied towards design of PVC plastisols with improved properties.

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