

# High-Temperature Stabilization of Polyolefines with Hydroxides of Alkali Metals

YU. P. LOSEV\* and Ya. M. PAUSHKIN

V. I. Lenin Byelorussian State University, Universitetskii Gorodok (Campus), 220080 Minsk, Byelorussia, CIS

## SYNOPSIS

Hydroxides of alkali metals are shown to be high-temperature stabilizers of polyethylene. Potassium hydroxide is found to be most efficient. The reaction mechanism of alkali metal hydroxides as thermal stabilizers is considered.

## INTRODUCTION

Polyolefines are one of the main types of synthetic polymer materials. However, an important shortcoming is their low temperature resistance and heat stability, which reduce the processing efficiency and restrict their range of application.

So far the study of high-temperature stabilization of polyolefines has been limited since solution of the problem involves some difficulties. In the case of polyolefine the use of stabilizers against thermal and light-oxidative degradation is not efficient since at high temperatures they easily decompose to form radical capable of initiating additional kinetic destruction chains.

To date, few antioxidants and light stabilizers have been found that can partially inhibit thermal destruction of polyolefines.

## EXPERIMENTAL

Inhibition of thermal decomposition of hydrocarbons was investigated in a flow-type installation, which is a hollow cylinder made from stainless steel with a volume 950 cc, equipped with electric heating. Hydrocarbon was fed from a calibrated reservoir into a coil evaporator and then entered into the reaction vessel at a given temperature, where it contacted the inhibitor. Products of the reactions entered a condenser and then a receiving vessel; noncondensed

gases pathed through a "gas clock" for determining volume and then discharged into the atmosphere. Experiments under pressure were conducted in a microautoclave with a working volume of 10 cc. Hydrocarbon was allowed to stand at the temperature of the experiment during the given time; then the microautoclave was cooled, and pyrogas was collected, using a valve, in a gas buret. The quantity of nondecomposed hydrocarbon was determined by GLC on LXM-7A according to the following procedure:

Detector—catharometer; gas carrier—helium; length of the column 2 m, sorbent 3% squalene on activated aluminum oxide, treated with 3% solution of sodium hydroxide; speed of the gas carrier was 35 mL/min; temperature of the column 75°C.

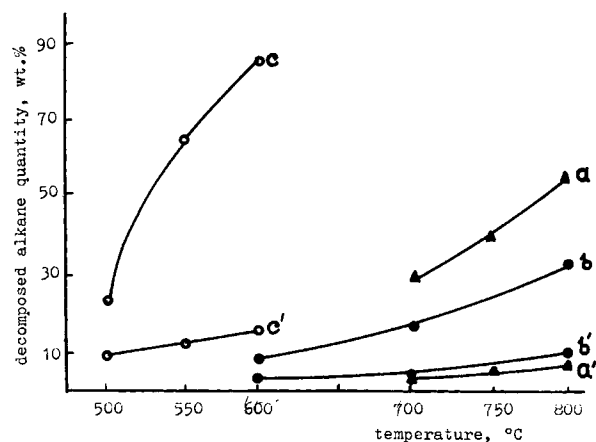
Inhibition of the thermal destruction of polyolefines was investigated in glass tubes in a continuous nitrogen stream, to remove volatile products of destruction by an ampule method at  $10^{-4}$  Torr. After heating at the temperature of the experiment, the viscosity-average molecular weight was determined with the intrinsic viscosity for polyethylene in decalin at 85°C.  $K = 3.873 \times 10^{-4}$ ,  $\alpha = 0.738$ , and mass loss

$$\alpha = g/g_0$$

where  $g$  is the change of the weight of the specimen after decomposition.

Determination of the change of the concentration of double bonds was carried out on films with thickness 500 m and degree of branching 50 m by IR spectroscopy (Spectrophotometer UR-20). Spectra are taken in the range of 850–1050  $\text{cm}^{-1}$ . Optical

\* To whom correspondence should be addressed.



**Figure 1** Temperature effect on thermal decomposition of alkanes: (a) heptane without inhibitor; (a') inhibitor Na; (b) heptane without inhibitor; (b') BAU coal-supported KOH inhibitor; (c) hexadecane without inhibitor; (c') BAU coal-supported KOH inhibitor.

density of the absorption bands D 888 (RR' — CH=CH<sub>2</sub> vinylidene; 909 RCH=CH<sub>2</sub> vinyl, 965 RCH=CHR — *trans*-vinyl).

## RESULTS AND DISCUSSION

For the first time, the possibility of 6 high-temperature stabilization of polyolefines was demonstrated with low-molecular models, normal-structure alkanes.<sup>1-3</sup> It was found that 12-15 S contact with metallic sodium and potassium hydroxide supported on BAU coal carrier efficiently inhibited the thermal decomposition flowing *n*-heptane at 800°C (Fig. 1). The inhibitors of thermal destruction of hydrocarbons such as olefines and nitrogen protoxide, described in the literature, appear ineffective under these conditions.

In the hexadecane case the supported potassium hydroxide is efficient as an inhibitor to 600°C (Fig. 1). The effective inhibition of *n*-alkane cracking by metallic sodium and potassium hydroxide on the BAU coal carrier was also observed under pressure for 2 h (Table I).

At 500°C, metallic sodium causes almost complete inhibition of the heptane and hexadecane cracking for 120 min. In the presence of BAU-supported potassium hydroxide, the decomposed hydrocarbon fraction is 2.6% for heptane and 3.1% for hexadecane. Hydrides and amines of alkali metals exhibit a high efficiency as inhibitors of thermal decomposition of *n*-alkanes.<sup>4-6</sup>

In the case of polyethylene, supported potassium hydroxide is efficient as a thermal stabilizer to 440°C (Fig. 2). As regards their efficiencies, the alkali metal hydroxides as thermal stabilizers of polyethylene may be arranged in the series: KOH > NaOH > LiOH (Fig. 3). Potassium hydroxide inhibits the thermal decomposition of olefines different degrees (Table II).

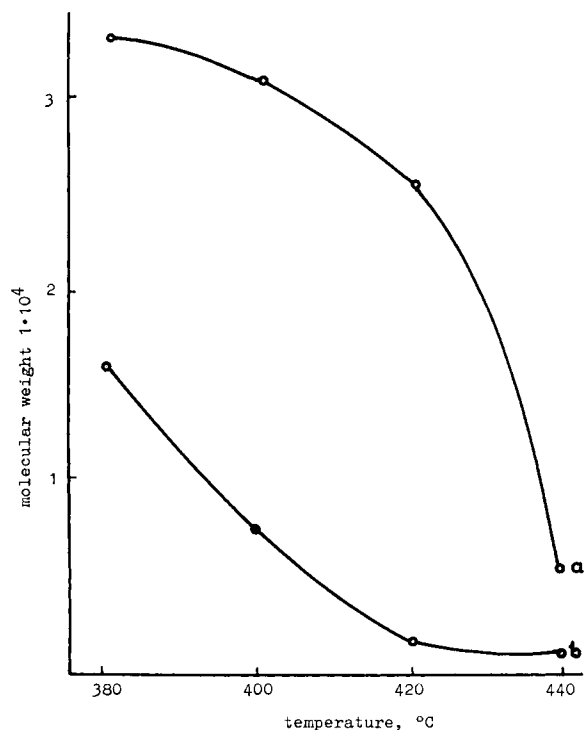
The effect of inhibition by BAU coal-supported potassium hydroxide was observed for all polyolefines, but to a different degree. The thermal destruction of polypropylene is inhibited insignificantly because degradation follows a mechanism involving mainly hydrogen transport, and only a small fraction of polypropylene decomposes following the radical mechanism that inhibited. The polyethylene decomposition takes place following the radical mechanism, which involves a breakdown of the carbon-carbon chain in accordance with the law of probability, and the inhibition effect is considerable.

Hydroxides of alkali metals are also efficient inhibitors of thermal destruction of carrier-free polyolefines but at lower temperatures (Table III).

Potassium hydroxide completely inhibits the thermal destruction of high-pressure and low-pres-

**Table I** The Inhibition of *n*-Heptane and Hexadecane Cracking under Pressure in an Autoclave (500°C, 120 min)

Inhibitor	Gas Evolution (wt %)	Cracking Product Percentage (wt %)	Decomposed Hydrocarbon Percentage (wt %)
Heptane without inhibitor	45.2	11.5	56.7
Heptane with sodium	2.1	—	2.1
Heptane with BAU coal-supported KOH	2.5	0.1	2.6
Hexadecane with sodium	2.3	—	2.3
Hexadecane without inhibitor	49.3	15.6	64.9
Hexadecane with BAU coal-supported KOH	2.8	0.3	3.1



**Figure 2** Temperature effect on thermal destruction of polyethylene: (a) without inhibitor; (b) BAU coal-supported KOH inhibitor.

sure polyethylene with molecular weight 34,800. In the case of high-molecular polyethylene, the molecular weight decreases by 1.8; without an inhibitor the decrease is 7.5-fold.

With increasing concentrations the weight loss drastically diminishes [Fig. 4(a)], and a relative molecular weight reaches its maximum at 5% KOH concentration [Fig. 4(b)].

The molecular weight of polyethylene undergoing thermal degradation in the presence of potassium hydroxide changes at a lower rate than without it (Fig. 5).

At 300°C with potassium hydroxide, molecular weight of polyethylene is found to increase, i.e., macropolymerization takes place.<sup>5,6</sup> At 350–375°C, potassium hydroxide efficiently inhibits the thermal destruction of polyethylene. The relative change of the molecular weight is two or three times lower than that without inhibitor. At 400°C, the inhibitor efficiency is insignificant. The BAU coal-supported potassium hydroxide is efficient up to 440°C, which may be explained by the large contact surface area of inhibition of macroradicals.

Glass fiber is a high-temperature thermal stabilizer of polyethylene. It is efficient as a thermal degradation inhibitor to 400°C. The inhibition effi-

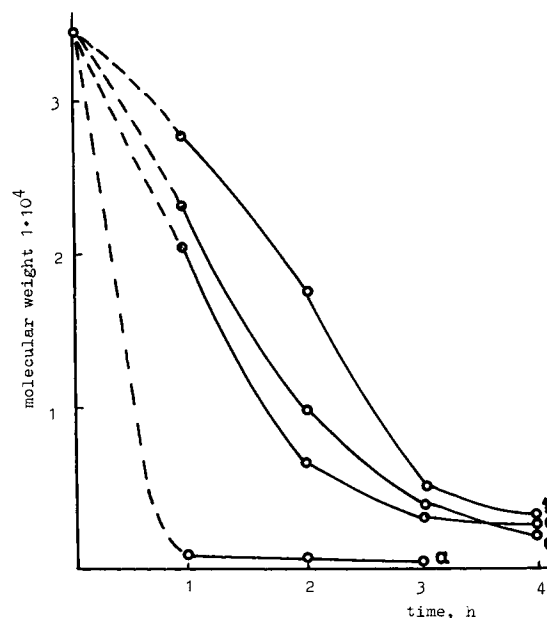
ciency rises as sodium oxide content increases from 0.7 to 16% (Fig. 6).

Similar behavior is observed in studies investigating the effect of time on the inhibition of thermal destruction of polyethylene with glass fiber of different compositions (Fig. 7). At 350°C and 6-h exposure in the presence of 30% glass fiber containing 16% sodium oxide, the molecular weight of polyethylene does not actually change whereas without an inhibitor it decreases sevenfold. The use of alkali glass fiber as a filler makes it possible to prepare glass plastics on the basis of common and vulcanized polyethylene of higher thermal stability.

### PROPOSED MECHANISM

Alkali metals and hydroxides of alkali metals are inhibitors of thermal decomposition of polyolefines following the radical-chain mechanism. They do not inhibit the thermal depolymerization of polystyrene that follows a molecular mechanism and exhibit a low efficiency while inhibiting the thermal destruction of polypropylene that follows mainly the hydrogen transport mechanism.

In hydroxide of alkali metals under the thermal motion effect and during the endothermal transition of an electron from ion  $\text{OH}^-$  onto  $\text{Me}^+$ , Me and OH



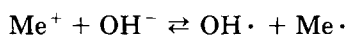
**Figure 3** Time effect on thermal destruction of polyethylene: (a) without inhibitor; (b) BAU coal-supported KOH inhibitor; (c) BAU coal-supported NaOH; (d) BAU coal-supported LiOH.

**Table II The Inhibition of Thermal Destruction of Polyolefines by BAU-Supported Potassium Hydroxide in Nitrogen Atmosphere<sup>a</sup>**

Polyolefines	Molecular Weight before Destruction	Molecular weight after Destruction	
		Without Inhibitor	BAU-Supported KOH
Low-pressure polyethylene	34,800	4000	18,700
Low-pressure polyethylene	158,000	1050	9,500
High-pressure polyethylene	37,500	2100	15,000
Medium-pressure polyethylene	63,000	5750	353,000
Polypropylene	366,400	900	2,300

<sup>a</sup> 420°C; 120 min; polyolefine/inhibitor = 1/1. Note: The KOH quantity is 0.51 g mol per 100 g of BAU coal.

radicals are formed. As a result, on the inhibitor surface free valencies appear, the concentrations of which are defined by the balance



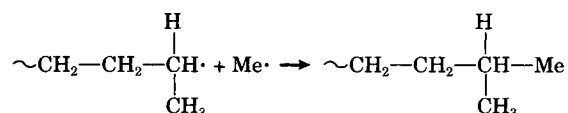
Different efficiencies of alkali metal hydroxides are probably associated with the differences in the ionization potentials.

According to the value of the ionization potential and electronic work, the alkali metals may be arranged in the series: Li Na K, whereas, as regards their efficiencies, as inhibitors of thermal destruction of polyolefines, the hydroxides are arranged as follows: KOH > NaOH > LiOH. The alkali metals are arranged according to their efficiencies in the following series: Na > K > Li. This may be ascribed to the fact that the electronic work function from sodium slightly exceeds that from potassium. But the sodium atomic size is considerably smaller, and therefore a sodium radical more efficiently accepts macroradicals which are formed during thermal destruction of polyethylene than does a potassium radical.

The efficiency of inhibition by alkali metal hydroxides increases with polyethylene branching.

This is supported by the fact that hydroxides of alkali metals decrease the propane and propylene yields to a greater extent than those of ethane and ethylene. The decrease of the propane and propylene yields may be explained by the fact that hydroxides of alkali metals inhibit the isomerization stage of macroradicals more efficiently. In polyethylene degraded in the presence of inhibitors, the contents of vinylene (965 cm<sup>-1</sup>) and vinylidene (888 cm<sup>-1</sup>) vinyl (909 and 965 cm<sup>-1</sup>) bonds considerably decrease. The total unsaturation of polyethylene degraded with an inhibitor increases by a factor of 1.5, but the branching appears markedly reduced.

The first stage of the inhibition of thermal destruction of polyethylene is proposed to be metalation of the polyethylene macroradicals with a metal radical:

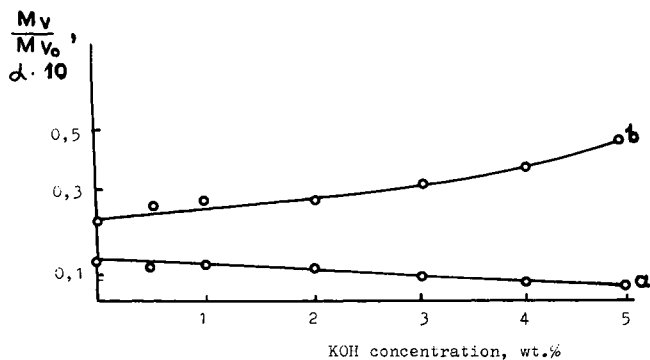


It might seem that hydroxides of alkali metals inhibit the thermal destruction of polyethylene in accordance with the scheme

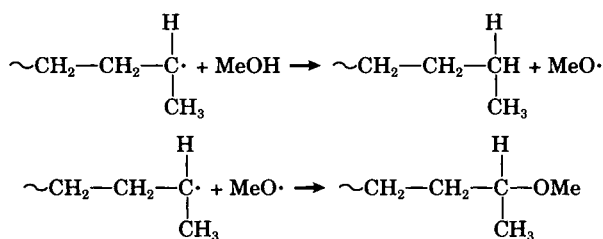
**Table III The Inhibition of Thermal Destruction of Polyolefines by Potassium Hydroxide<sup>a</sup>**

Polyolefines	Molecular Weight		
	Before Destruction	After Destruction	
		Without Inhibitor	With Inhibitor
Low-pressure polyethylene	158,000	21,000	86,200
Low-pressure polyethylene	34,800	12,750	37,000
High-pressure polyethylene	37,500	13,600	37,600
Polypropylene	366,400	161,800	253,400

<sup>a</sup> 350°C; 120 min; 5% KOH concentration.

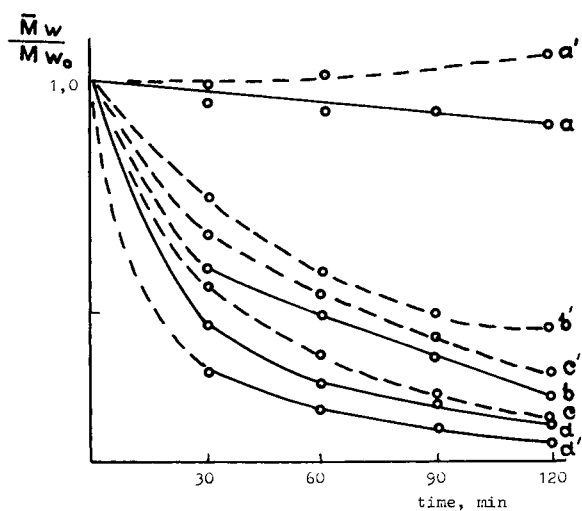


**Figure 4** The effect of potassium hydroxide concentration on the weight loss (a) and relative molecular weight (b).

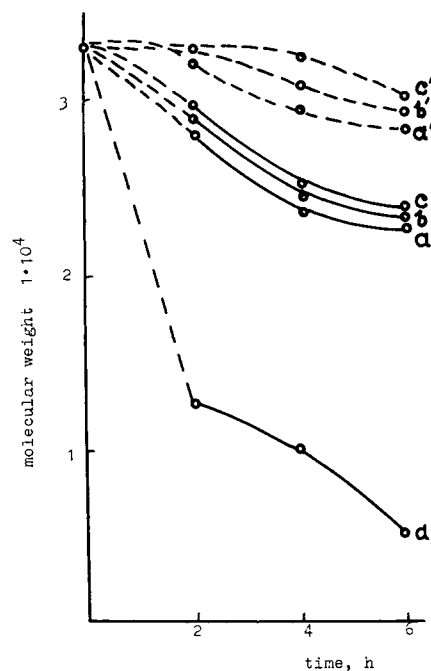


by analogy with phenol inhibition.

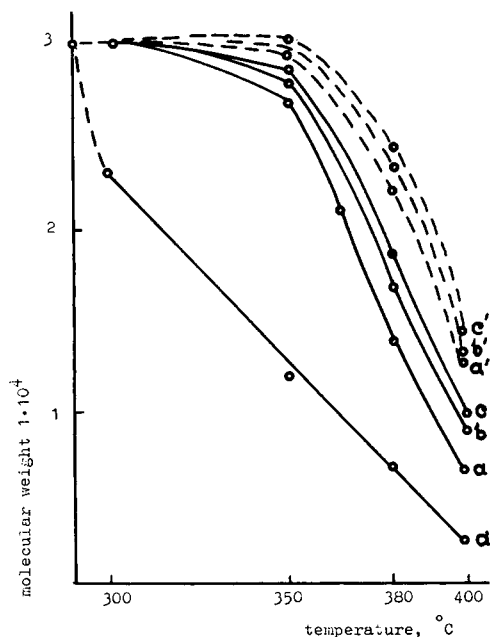
However, this mechanism is not consistent with the facts: (1) a high strength of the HOME bond (90 kcal/mol) considerably exceeds that of OH bond in phenol molecules, which excludes its breakdown at 350–400°C; (2) the absence of absorption bands at 700–900 cm<sup>-1</sup> in the IR spectra after polyethylene destruction that are characteristic of the C–O–Me bond; (3) the absence of an EPR signal in the destruction products.



**Figure 5** The effect of temperature and time on the relative molecular weight of polyethylene: (a–d) without inhibitor; (a'–d') with 5% KOH; (a, a') 300°C; (b, b') 350°C; (c, c') 375°C; (d, d') 400°C.



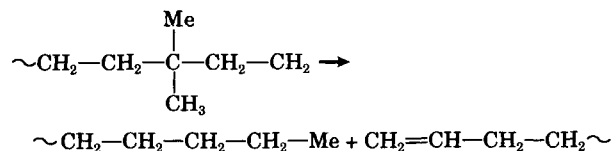
**Figure 6** The inhibition of thermal destruction of polyethylene by glass-fiber filler at different temperatures (120 min) Filler content: (—) 10%; (---) 30%. The quantity of Na<sub>2</sub>O (wt %): (a, a') 0.7; (b, b') 11.5; (c, c') 16.



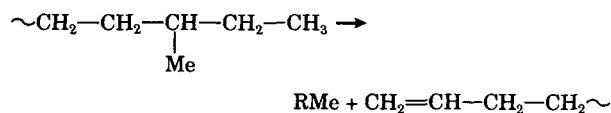
**Figure 7** Time effect of the inhibition of thermal destruction of polyethylene by glass fibre filler (350°C, in vacuum). Filler content: (---) 10%; (---), 30%. Na<sub>2</sub>O content (wt %): (a, a') 0.7; (b, b') 11.5; (c, c') 16. (d) Without inhibitor.

That thermal destruction of polyethylene is inhibited by alkali metals supports metallization of a macroradical.

The metal alkyl decomposition takes place at the second stage. Metal alkyl can decompose into metal alkyl and olefine which increases the unsaturation of polyethylene macromolecules:



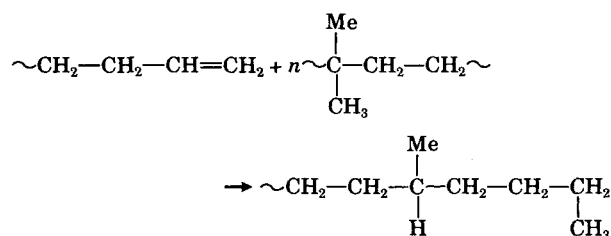
The decomposition of metal alkyl may also involve the breakdown of the carbon-carbon bond at the  $\beta$ -site in the C-Me bond:



where R = C<sub>1</sub>-C<sub>3</sub>.

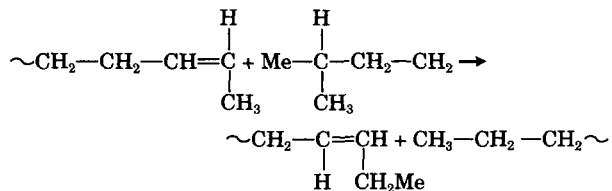
The above reaction drastically reduces the amount of methyl group in polyethylene and increase the quantity of double bonds. The metal alkyl formed rapidly decomposes at 200-250°C to give alkali metal, alkanes, and alkenes, C<sub>2</sub>-C<sub>3</sub>.

The metal alkyl can react with the unsaturated ends of polyethylene molecules:



It is noteworthy that the breakdown of polymer chain is hindered and the macromolecular sizes are even increased at temperatures up to 300°C.

Metal alkyl can react with unsaturated macromolecular ends in the substitution reaction type:



which also decreases the contents of methyl groups.

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