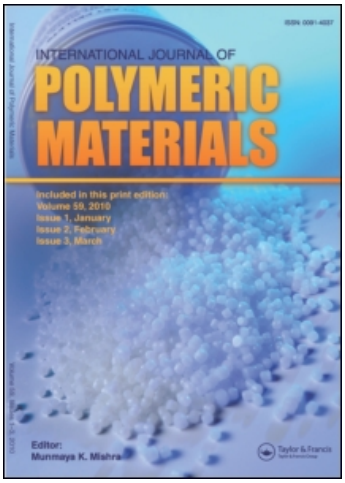

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

On The Color Change of Stabilized With Topanol CA and Santowhite Crystals Polyethylene Upon Aging

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To cite this Article Rakovski, S. K. , Kasparov, V. V. , Parfenov, V. M. and Popov, A. A.(1990) 'On The Color Change of Stabilized With Topanol CA and Santowhite Crystals Polyethylene Upon Aging', International Journal of Polymeric Materials, 13: 1, 223 — 226
To link to this Article: DOI: 10.1080/00914039008039477
URL: http://dx.doi.org/10.1080/00914039008039477

Intern. J. Polymeric Mater., 1990, Vol. 13, pp. 223–226
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Printed in the United Kingdom

On The Color Change of Stabilized With Topanol CA and Santowhite Crystals Polyethylene Upon Aging

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The granulated polyethilene (PE) stabilized with Topanol CA and Santowhite crystal grows yellow after one year-long storage. The same samples of PE stabilized with Ionol and Santowhite crystals preserves its white color. The yellow coloring reduces the commercial value of the PE.

The study has been accelerated by initiated oxidation of cumene and *n*-decane in presence of the three stabilizers and their mixtures. The visible range spectra of oxidates were established to have a characteristic absorption at 400 nm only in the presence of the Topanol CA. Such absorption is to be observed also in the PE stabilized with Topanol CA after storage. The other two stabilizers do not change the spectra at 400 nm. It was found from the analyses of oxidating Topanol CA that the three compounds with quinoic structure are formed, and they are reasons for the coloring of PE.

KEYWORDS: Topanol CA, santowhite, degradation, polyethylene, changing of color, mechanism

INTRODUCTION

The phenol type stabilizers like 2,6-di-*tert*-butylphenol (Ionol) find wide application in the production of polyethylene (PE). One of the newest stabilizers, produced by ICI 1,1,3-tris(5′-*tert*-butyl-4′-hydroxi-2′-methylphenyl)butane (Topanol CA) is being used recently. It is the most effective phenol tupe stabilizer with relatively lower volatility (melting point 188°C) and water solubility.[1] This makes it very suitable for use in relatively smaller amounts (up to 0.5%) for stabilization of polyolefines, including PE.

The PE has to be stabilized additionally in some productions where it is applied. Most often 4,4′-thio-bis-(6-*tert*-butyl-*m*-cresol) (Santowhite crystals, SC) is used as a stabilizer in concentrations from 1 to 3 wt.%.

When PE is stabilized with 0.5 wt.% Ionol and 1 wt.% SC the color of the PE

granules remains white for 1 year, while if the first stabilizer has been Topanol CA (0.5 wt.%) after a period of 1 year the PE granules turn yellow.

The aim of the present paper was to find the reason for this phenomenon and to indicate the ways of its overcoming.

EXPERIMENTAL

Stabilizers

Ionol product of USSR, Topanol–ICI, and Santowhite crystals–MO were industrial samples without additional purification.

Substrates

Cumene and *n*-decane were p.a. grade. They were purified as described in[2].

Polymers

The high density polyethylene was produced in Bulgaria. Four samples were prepared from this PE: The first one was stabilized with 0.5 wt.% of Ionol, the second—with 0.5 wt.% of Topanol, the third and the fourth were in the same way like the first two, but additionally stabilized with 1 wt.% of SC.

Methods

An initiated oxidation of cumene or *n*-decane at 363 K with 0.1 M dicumene-hydroperoxide (DCHP) in the presence of the above three stabilizers and their

TABLE I

Inhibited oxidation of cumene at 363 K, inhibited by DCHP

No.	Topanol CA mM	Ionol mM	SC mM	Rel. rate	Time of oxidn min	$D_{\lambda=300}$
1	—	—	—	1	260	0.36[a]
2	1.0	—	—	20	192	0.88
3	0.5	—	—	11	93	0.58
4	0.1	—	—	3	113	0.28
5	—	1.0	—	5	150	0.22
6	—	—	1.0	18	78	0.43[a]
7	0.1	—	0.4	8	420	0.83
8	0.2	—	0.3	9	480	0.96
9	0.2	—	0.2	7	396	0.58
10	0.25	—	0.25	9	330	0.56
11	0.4	—	0.1	10	307	0.87

[a] Background.

mixtures was used.[3] The uv–vis ir, nmr, and mass spectra were recorded on the Specord UV–VIS, Specord 711R, Brucker WM-250 and Jeol, JMS D300, respectively.

RESULTS AND DISCUSSION

The results from cumene oxidation in the present of the stabilizers and their mixtures are represented in Table I. Topanol CA was established to be the most effective of the three stabilizers, then follows SC and Ionol. The relative efficiency of Topanol CA is 4 times greater than that of Ionol and 1.25 times higher than of the SC. The oxidates' spectra are represented in Figure 1.

The number of the spectra correspond to the experiments from Table I. It can be seen that upon oxidation in presence of Topanol CA a peak appears with a maximum at 400 nm, while with the other two stabilizers no such maximum is observed. Altogether with the increase of the cumene oxidation degree background of the spectrum is increased at a rate of 1.38×10^{-3} density units per min, but in the presence of Topanol CA the rate is 3.62 times bigger. The results in the presence of the three stabilizers, when *n*-decane is oxidized, are similar. When the spectra of a PE film are compared with the spectrum of the oxidate a similarity is to be noticed in the spectral bands at 400 nm. These data allow us to conclude, that Topanol CA is responsible for the yellow coloring. Analyzing the structure of the compounds, formed upon Topanol CA oxidation we can draw the

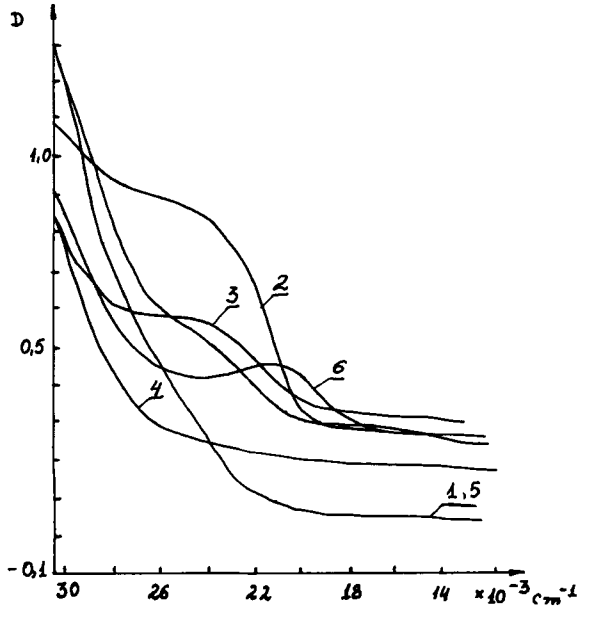
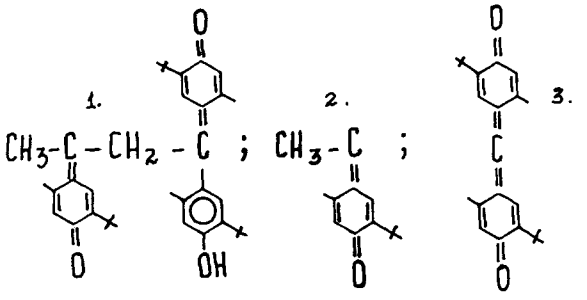


FIGURE 1 Visible spectra of oxidates. The cell length is 1 cm.

conclusion that their structure is the following:



The structure 3 has a very high value of the extinction coefficient of the order of $10^5\,M^{-1}\,cm^{-1}$.

As a result of the conducted study we propose to exclude the use of stabilizers, allowing the formation of structures of type 3, with the aim to stabilize the PE so that it does not change its color.

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