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STUDY OF THE SYNTHESIS OF BIS-CARBAMATE OF THE MEE SERIES AND STUDY OF BRUTTO INHIBITORY ACTIVITY

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Abstract. This research work is devoted to the synthesis of a new bis-carbamate N,N'-hexamethylene bis-[(ortho-cresol)-carbamate] i.e. MEE-1 based on diisocyanates and cresols. A possible mechanism of inhibited oxidation for polymers in two stages has been proposed. And also, the brutto (gross) inhibitory activity in model reactions of thermal autoxidation of low-density polyethylene was studied. As a result, it turned out that MEE-1 bis-carbamate increases the thermal-oxidative stability of low-density polyethylene by 2.5-43.2 times compared to other industrial antioxidants and arouses practical interest for further study.
Key words: Bis-carbamate, amines, proton, inhibition, oxidation, radicals, polyethylene, ionol, initiator, induction.

Introduction. Esters of carbamic acids - urethane and carbamate compounds with the general formula R'R''NCOOR, are widely used in various industries. Representatives of this class of chemical compounds exhibit broad biological activity, due to which they are used as additives (antioxidants and corrosion inhibitors), medicines (for example, proserin and carbacholine) and plant protection products (herbicides, fungicides, insecticides, acaricides and plant growth stimulants) [1-4]. In recent years, increased interest in bis-carbamate compounds is associated with the possibility of use in a variety of fields. Polyurethanes are widely used in industry, used in the form of urethane rubbers, polyurethane adhesives, varnishes and fibers [5-7]. The authors of this work synthesized about twenty bis-carbamate compounds and used them as a metal corrosion inhibitor, a fuel antioxidant, and a plant biostimulator [8-10]. Scheme for the synthesis of N,N'-hexamethylene-bis-[(o-cresol)-carbamate] i.e. MEE-1:

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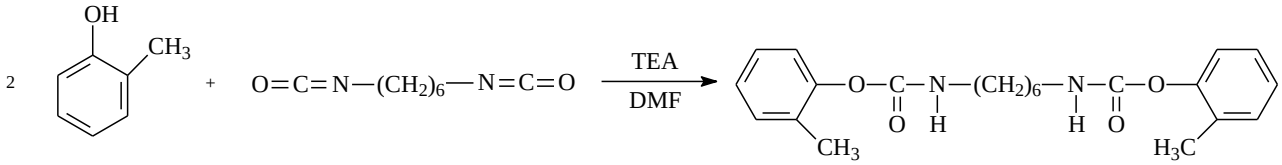

The nitrogen and oxygen atoms in the –N=C=O group of hexamethylene diisocyanate (HMDI) are primarily negatively charged and electron-donating, making this group susceptible to both nucleophilic and electrophilic attacks. In some cases, diisocyanates can also act as electrophilic agents. The most typical reactions for them are nucleophilic addition reactions involving oxygen and nitrogen-containing substances [11-13, 17-22]. The presence of an amine group in the MEE-1 bis-carbamate molecule indicates the possibility of its use as an antioxidant for polymers, which is also reflected in foreign literature [14-16]. Aging of polymer materials is a change in the composition of the material due to chemical transformations under the influence of atmospheric oxygen (auto-oxidation) or free radicals formed. Antioxidants are substances introduced into a polymer composition to prevent its aging. Also, antioxidants belong to a large group of polymer stabilizers [23,24].

The purpose of this research work is to study bis-carbamate MEE-1 as an antioxidant for low-density polyethylene.

Materials and Methods. Preparation of N,N'-hexamethylene bis-[(ortho-cresol)-carbamate]: To 8.40 g (0.1 mol) of ortho-cresol, 10 ml of triethylamine (TEA), 35 ml of dimethylformamide (DMF), at While stirring, add dropwise at room temperature 8.42 ml (0.05 mol) of hexamethylene diisocyanate dissolved in 20 ml of DMF. The reaction mixture is stirred for 3.0-4.0 hours at a temperature of 35-45 °C; after the time has elapsed, the contents of the flask are transferred to a glass and water is added. The resulting precipitate is washed with thin layer chromatography (TLC). After drying, a snow-white powder is obtained; the product yield is 18.74 g (97.6% of theoretical). The brutto (gross) inhibitory activity of bis-carbamate MEE-1 was studied in model reactions of thermal autoxidation of polyethylene (PE, 190 °C, [AmH] = 4.0 μmol/g). Ionol and 2,4,6-trimethylphenol (TMP) were used as reference standards.

Results and Discussions. The mechanism of action of the most common antioxidants (aromatic amines, phenols, naphthols, etc.) is the termination of

reaction chains: antioxidant molecules interact with active radicals to form low-active radicals. The MEE-1 bis-carbamate molecule contains two functional amino groups (AmH):

$$R^1–O–CO–NH–R–NH–CO–O–R^1$$

where R^1 is an aromatic ring; R – hexamethylene.

Accordingly, at the first stage it is necessary to study the mechanism of oxidation in a hydrocarbon environment, and at the second, the mechanism of action of the antioxidant in this environment. Table 1 suggests a possible mechanism of inhibited oxidation for low-density polymers in two stages:

Table 1

Mechanism of inhibited oxidation for low-density polymers

Stage 1: Oxidation in a hydrocarbon environment	Stage 2: Mechanism of action of the antioxidant
$RH + O_2 \rightarrow R^{\cdot} + r$	$AmH + RO_2^{\cdot} \rightarrow Am^{\cdot} + ROOH$
$I \rightarrow 2er_i^{\cdot}$	$Am^{\cdot} + ROOH \rightarrow AmH + RO_2^{\cdot}$
$RH + r^{\cdot} \rightarrow R^{\cdot} + rH$	$AmH + R^{\cdot} \rightarrow Am^{\cdot} + RH$
$RH + r_i^{\cdot} \rightarrow R^{\cdot} + r_iH$	$AmH + r_i^{\cdot} \rightarrow Am^{\cdot} + r_iH$
$O_2 + R^{\cdot} \rightarrow RO_2^{\cdot}$	$Am^{\cdot} + RO_2^{\cdot} \rightarrow$ продукт
$RH + RO_2^{\cdot} \rightarrow R^{\cdot} + ROOH$	$Am^{\cdot} + RO_2^{\cdot} \rightarrow AmH +$ product
$ROOH \rightarrow 2r^{\cdot}$	$Am^{\cdot} + Am^{\cdot} \rightarrow Am–Am$
$ROOH \rightarrow$ product	$Am^{\cdot} + RH \rightarrow AmH + R^{\cdot}$
$RO_2^{\cdot} + RO_2^{\cdot} \rightarrow O_2 +$ product	-

*Note: Where RH is the oxidizing medium, I is the initiator, e is the probability of initiator radicals entering the volume, $r^{\cdot}$ is a radical of any structure other than $r_i^{\cdot}$, $R^{\cdot}$, $RO_2^{\cdot}$.

Also, during the process of inhibited oxidation, $AmO^{\cdot}$, AmOH, AmOR and other products of the transformation of the original carbamate amines are formed in the system, which, in principle, can have inhibitory or initiating activity. However, theoretical studies of the antioxidant activity of bis-carbamate MEE-1 to polymer products must be verified in the course of determining the kinetic parameters by experimental studies. Testing The gross inhibitory activity of bis-carbamate MEE-1 was studied in model reactions of thermal autoxidation of polyethylene (PE, 190 °C, [AmH] = 4.0 μmol/g) using manometric and iodometric methods. Ionol and 2,4,6-

trimethylphenol (TMP) were used as reference standards. According to the results of the study, the bis-carbamate MEE-1 synthesized by us is superior in its ability to inhibit oxidative processes to well-known industrial antioxidants such as ionol and TMF (Table 2).

Table 2

Induction period of polyethylene oxidation inhibited by bis-carbamate MEE-1

Compound	τ, min.
	Polyethylene (PE)
MEE-1	216±5
Ionol	87±5
TMP	80±5
Control	5

In accordance with the data obtained (Table 2), the studied bis-carbamate MEE-1 has a pronounced inhibitory effect on the oxidation of polyethylene. Bis-carbamate MEE-1 increases the thermal-oxidative stability of low-density polyethylene by 2.5-43.2 times compared to other industrial antioxidants.

Conclusion. Primary antioxidants include aromatic amines, as well as alkylphenols - all of these substances act as a hydrogen donor. This group includes both secondary amines and diamines, as in our bis-carbamate molecule MEE-1. In this regard, one could assume the likelihood of the antioxidant properties of this substance. Having studied the world's literature research, we think that they will be very effective in heat aging, but are not suitable for the preparation of light-colored polymer mixtures due to persistent and irreversible darkening in the light. Thus, when studying the gross inhibitory activity of bis-carbamate MEE-1, it was revealed that it increases the thermal-oxidative stability of low-density polyethylene by 2.5-43.2 times compared to other industrial antioxidants. In general, the results of studies of the synthesized bis-carbamate MEE-1 allow us to conclude that these compounds are of practical interest as inhibitors of the oxidation of polymers, fuels and lubricants, and we believe that it is necessary to continue research.

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