**Bifunctional Nickel- or Cobalt-containing Catalyst-stabilizers for Polybutadiene Production and Stabilization: (Part II)-Antioxidative Properties and Mechanism of Catalyst-Stabilizer’s Action in the Processes of Thermo- and Photooxidative Ageing of Polybutadiene**

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Received 26 May 2002; accepted 10 April 2003

**ABSTRACT**

The analysis of literature data has given strong evidence that the use of Ni and Co-organic dithioderivatives, as components of bifunctional catalysts, not only catalyzes the polymerization process, but it protects the system from oxidative ageing as well. As part of the continuing work of the first part for the present research work, studies have been carried out on the stabilizing properties of cobalt-containing catalytic dithiosystems (Co-dithiophosphates + DEAC) in the processes of 1,4-cis polybutadiene (PBD) thermal and photodegradation. To reach the most effective combination of the catalytic and stabilizing properties of catalysts, it is necessary to introduce into the complex the ligands of functional groups and the dithio groups as well to provide synergistic effect of thermo and photooxidative stability. The above system’s effectiveness has been confirmed to surpass the activity of the pure cobalt dithiophosphates and the antioxidant Agidol (NG-2246) used in industry.

Iranian Polymer Journal, 12 (4), 2003, 281-289

**INTRODUCTION**

All polymeric materials including polydienes (polybutadienes, polyisoprenes, etc.) in the processes of storage, conversion and exploitation are subjected to the irreversible processes of destruction leading to sharp deterioration of their physico-chemical and mechanical properties, and decrease of their lifetime.

The main degradation factors are the actions of heat, radiation, oxygen, ozone, mechanical loads, etc. The rate of degradation is affected not only by the intensity of destruc-
tive factors, but, in some cases, mainly by the functional groups and variable valence metals in the polymeric matrix, initiating and sensitizing processes of degradation.

The existing cobalt-and nickel-containing catalytic systems used in the process of PBD preparation lead to the same results. Their residues in the polymer favour its oxidation and cross-linking. To prevent it happening, after polymerization process the PBD is carefully washed to remove the catalyst residues with subsequent stabilization using the special antioxidants. This leads to the complexity of the production flowchart, to great expenditures of energy and labour and the great problem is the formation of considerable amounts of wastes, containing the harmful metal ions that pollute the ecological sphere around the production.

It has been established by us that metal-containing dithioderivatives in combination with organo-aluminium compounds are highly active catalyzing systems for butadiene polymerization (Part I of this paper). N.F. Janibeyov and coworkers, based on metal-containing dithiosystems, developed the highly efficient multifunctional stabilizers for polymers [1]. The above-mentioned findings became the scientific premises for the creation of the bifunctional catalyst-stabilizers based on metal-containing dithiocompounds having no analogs for PBD preparation process with simultaneous stabilization of the end polymer.

In the present paper the summaries of the results of the researches are presented, which were earlier carried out in IPCP of the Azerbaijan National Academy of Sciences in the field of study of antioxidative properties of catalyst-stabilizers for butadiene polymerization on the basis of cobalt dithioderivatives and alkylaluminium halogenides against 1,4-cis-PBD thermo- and photooxidative ageing.

EXPERIMENTAL

The full account of the experimental section is given in part I of this two-part paper [9].

RESULTS AND DISCUSSION

The analysis of the above literature data allowed convincing viability of our concepts, who first proposed to use Ni- and Co-organic dithioderivatives as components of bifunctional catalysts for butadiene stereoregular polymerization capable not only to catalyze the polymerization process but to protect it from oxidative ageing. Further, these conceptions have been confirmed by the data of previous works [10-18]. However, for the first time in the present research there has been an attempt to generalize the results of the investigations on study of the bifunctional catalyst-stabilizers in the processes of thermo- and photooxidative ageing of polybutadiene.
The PBD compositions have been studied with:

a) individual dithioderivatives of Co\textsuperscript{2+} (DTD-Co);
b) catalytic system- DTD-Co + diethylaluminium chloride (DEAC);
c) mixture of catalytic system + Agidol;
d) pure commercial stabilizer Agidol.

The efficiency of dithiophosphates stabilizing effects was determined by the method of inhibiting the polybutadiene thermo-oxidative ageing [20] and its oxidative ageing in thin films [21].

The thermo-oxidative ageing was carried out at temperatures 80°C and 140°C, oxygen pressure 200 mm Hg. The process was observed through oxygen absorption in monometric unit.

The results of PBD-compositions thermo-oxidative degradation studies are set in Table 1, and the kinetic curves are depicted in Figure 1.

The kinetic curves analysis shows that both the induction period and the absorption rate in stationary section and the maximum amount of the absorbed oxygen depend on the composition's dithiocomponents nature.

It has been established that DTD-Co themselves are sufficiently strong antioxidants. They showed their stabilizing effect at far less concentrations (by 4-8 times) than Agidol. To judge by the induction period, oxidation rate and maximum amount of O\textsubscript{2} absorbed, the efficiency of their action strongly depends on the nature of surrounding metal ligand and falls in the following series:

X-Co >> CTPh-Co > 4-m-6-TBPh-Co > DEDTC-Co > NGDTPh-Co > DiPDTPh-Co

Somewhat different series of stabilizing efficiency is observed in the case of catalytic system DTD-Co + DEAC:

X-Co > NGDTPh-Co > 4-m-6 TBPh-Co > CTPh-Co > DEDTC-Co >> DiPDTPh-Co

As it is seen, the largest stabilizing activity is shown by X-Co, differed from the other compounds by the fact that, besides dithiophosphate fragments it contains, the screened hydroxyl group in the molecule.

The comparisons of dithiosystems with the starting dithiophosphates show that by the efficiency of the stabilizing effect the dithiosystems significantly surpass the pure dithiophosphates. It is noteworthy that a series of the stabilizing effects of the dithiosystems practically coincides with a series of their catalytic effects in butadiene polymerization process and this is an indication of the important role of dithiophosphate ligand showing both high catalytic and high stabilizing efficiencies of the dithiosystems.

The researches showed that all the systems at the temperature below 80°C fully inhibit the process of the thermo-oxidative degradation for 2 days. Upon increasing the temperature up to 140°C the behaviour of the oxyphenyl and oxydiisopropyl systems are sharply differed. In the last case the oxidation rate is not actually differed from the rate of the unstabilized polybutadiene oxidation.

It contradicts the known reality, the phenol antioxidants operate at lower temperatures, than sulphide-antioxidants.

The products of the catalytic systems conversion as well as the dithiophosphates themselves, have been established to be more effective oxidation inhibitors than the starting components. Principally such phenomenon has been described in literature. It has been shown in [20] that the hindered phenols in oxidation under the action of singlet oxygen are converted to the different stable products. The compounds obtained capable to catch easily the free radicals are generally rather more efficient inhibitors in the oxidation process than the starting phenols.

At present it is difficult to judge on the structures of dithiosystems oxidative conversion products. But it may be supposed that something similar occurs also in the case of dithiosystems as the results of the oxidation products are proved to be more efficient inhibitors, than the starting dithiosystems.

Particularly, this is strongly displayed in the case, where the hindered phenols fragments are conjugated with phosphorus-containing functional groups, the oxidative conversion considerably intensifies the stabilization effect of such polyfunctional stabilizers.

This seems to be the main reason that the systems with X-Co have the largest inhibiting power. With its presence the maximum amount of the absorbed oxygen is 2-8 times less than the other systems.

Thus, the experimental data and their analysis in the light of literature information show that the stabilizing efficiency of the dithiosystems is significantly connected with the ligand nature rather than transition metal atom.

One of the most important points of practical use of
the bifunctional catalyst-stabilizers is their compatibility with the conventional commercial antioxidants. To elucidate this point, there has been some studies on thermo-oxidative ageing of PBD composition containing the catalytic system DTD-Co + DEAC and Agidol (NG-2246). The latter was taken by 4-8 times higher than DTD-Co. The results obtained are presented in Figure 1c and Table 1.

It has been established that in all cases the catalytic dithiosystems in combination with Agidol show higher stabilizing effect. In this case the oxidation induction period increases, whereas, their rate decreases, which is the confirmation of their compatibility and synergism.

Thus, the catalytic dithiosystems are fully compatible with the commercial antioxidant-Agidol and it may be used in combination for polybutadiene stabilization from thermo-oxidative ageing.

Taking into account that PBD is usually stored at temperature not high than 40°C and at temperature below 80°C the PBD thermo-oxidation process cannot be investigated, there have been also studied the
processes of PBD photooxidation processes in films at room temperature under the effect of natural solar irradiation (scattered) using the method of IR-spectroscopy. The results of investigations are given in Figures 2-4.

The same PBD samples, which were used in the method of inhibited thermo-oxidative ageing, and exposure to photooxidation process just immediately after polymerization process followed by 2, 4, 7, 10 and 12 days time length.

The analysis of IR-spectra shows that in ageing of pure PBD the intensive photooxidation reactions occur, leading to the formation of hydroperoxide (hydroxylic) groups absorbing in region 3440 cm\(^{-1}\), carbonylic groups (C=O) in region 1720 cm\(^{-1}\) and ester (C-O, C-O-C) groups in region 1070 cm\(^{-1}\). As the ageing time increas-

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**Figure 2.** Kinetic curves of PBD cis-1,4-units intensity changes in PBD photooxidative ageing process and its compositions with: (a) catalytic system DTD-Co + DEAC and (b) synergetic mixture DTD-Co + DEAC + Agidol. Conditions: Room temperature; (1) PBD pure; compositions of PBD with catalytic system and synergetic mixture, where DTD-Co is: (2) CTPh-Co; (3) NGDTPh-Co; (4) 4m-6-TBPh-Co; (5) X-Co; (6) DEDTC-Co; (7) DIPDTPh-Co; (8) composition PBD + Agidol.

**Figure 3.** Kinetic curves of OOH/OH groups accumulation in PBD photooxidative ageing process and its compositions with: (a) catalytic system DTD-Co + DEAC and (b) synergetic mixture DTD-Co + DEAC + Agidol. Conditions are shown on Figure 2.
es the intensity of hydroperoxide and carbonylic groups absorption increases and the intensity of 1,4-cis-units absorption in region 740 cm\(^{-1}\) decreases.

The inter- and intramolecular hydrogen bonds between hydroxylic and neighbouring carbonylic groups lead to the appearance of arm in 3360-3400 cm\(^{-1}\) region.

As it is seen from Figures. 2a,3a,4a, in compositions containing PBD with its catalytic system the rates of OOH/OH, C=O groups accumulation and change of 1,4-cis-units content in a polymer sharply decreases as well. The rate of accumulation of these groups depends on the nature of dithiophosphate components of catalytic systems although this dependence is traced insufficiently clearly. Based on calculation of kinetics of OOH/OH and C=O groups formation as well as the change of 1,4-cis-units number the efficiency of the catalytic systems action may be arranged in the following averaged series:

X-Co > NGDTPh-Co > CTPh-Co 4-m6-TBPh-Co > DEDTC-Co > DiPDTPh-Co > PBD+Agidol

As it is seen, the efficiency series of the catalytic systems photostabilizing action does not practically differ from a series against thermooxidative destruction.

The PBD composition with catalytic system by its efficiency essentially surpasses the compositions with Agidol (Figures 2b,3b,4b).

The mixtures of catalytic systems with Agidol have rather more stabilizing efficiency than Agidol itself and this confirms synergism also in polybutadiene photooxidative ageing. The efficiency of the mixture catalytic system + Agidol depending on the cobalt-containing dithiophosphate nature, may be arranged in the following series:

X-Co > NGDTPh-Co > CTPh-Co > 4-m6-TBPh-Co > DEDTC-Co > DiPDTPh

The analysis of the results obtained and the literature data allows us stating some considerations concerning the mechanism of polybutadiene stabilization

<table>
<thead>
<tr>
<th>Item No</th>
<th>PBD Composition</th>
<th>(\tau_{\text{ind.}}) (min)</th>
<th>(W_{\text{O}_2}\cdot10^{-5}) (g/min)</th>
<th>Maximum amount of absorbed oxygen, (O_2\cdot10^{-3}) g/g of polymer</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PBD pure</td>
<td>3</td>
<td>20.2</td>
<td>7.3</td>
</tr>
<tr>
<td>2</td>
<td>Agidol (NG-2246)</td>
<td>110</td>
<td>1.2</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>X-Co</td>
<td>15</td>
<td>4.42</td>
<td>1.3</td>
</tr>
<tr>
<td>4</td>
<td>NGDTPh-Co</td>
<td>10</td>
<td>9.47</td>
<td>3.8</td>
</tr>
<tr>
<td>5</td>
<td>DEDTC-Co</td>
<td>10</td>
<td>8.32</td>
<td>3.5</td>
</tr>
<tr>
<td>6</td>
<td>4-m6-TBPh-Co</td>
<td>8</td>
<td>8.44</td>
<td>3.3</td>
</tr>
<tr>
<td>7</td>
<td>CTPh-Co</td>
<td>6</td>
<td>7.49</td>
<td>2.9</td>
</tr>
<tr>
<td>8</td>
<td>DiPDTPh-Co</td>
<td>4</td>
<td>17.9</td>
<td>5.8</td>
</tr>
<tr>
<td>9</td>
<td>X-Co + DEAC</td>
<td>40</td>
<td>1.04</td>
<td>0.5</td>
</tr>
<tr>
<td>10</td>
<td>CTPh-Co + DEAC</td>
<td>30</td>
<td>4.8</td>
<td>2.9</td>
</tr>
<tr>
<td>11</td>
<td>4-m6-TBPh-Co + DEAC</td>
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<td>2.56</td>
<td>2.2</td>
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<tr>
<td>12</td>
<td>NGDTPh-Co + DEAC</td>
<td>22</td>
<td>1.77</td>
<td>1.8</td>
</tr>
<tr>
<td>13</td>
<td>DEDTC-Co + DEAC</td>
<td>10</td>
<td>3.5</td>
<td>3.7</td>
</tr>
<tr>
<td>14</td>
<td>DiPDTPh-Co + DEAC</td>
<td>22</td>
<td>16.0</td>
<td>5.7</td>
</tr>
<tr>
<td>15</td>
<td>X-Co(C(_2)H(_5))(_2)AcI + Agidol</td>
<td>125</td>
<td>0.58</td>
<td>-</td>
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<tr>
<td>16</td>
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<td>130</td>
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<td>-</td>
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<tr>
<td>17</td>
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<td>0.16</td>
<td>-</td>
</tr>
<tr>
<td>18</td>
<td>4-m6-TBPh-Co + DEAC + Agidol</td>
<td>70</td>
<td>3.14</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 1. Comparison of the stabilizing efficiency of different PBD compositions.
in the presence of the catalytic dithiosystems.

It should be noted, above all, that as the results of the other authors' investigations showed [20], \(t\)-butylperoxide decomposition in the presence of cobalt dithiophosphates at temperatures below 50°C practically does not occur. Hence, the high stabilizing efficiency of cobalt catalytic dithiosystems, containing no phenol fragments, especially at low temperatures, cannot be connected with the compounds ability to decompose hydroperoxides. Thus, under these conditions the dithiosystems inhibit the processes leading to the formation of the primary radicals. The processes of polymer itself and oxygen electron-excited state are referred to them. In this process a special role is played by the dithiophosphate group. In this case the oxidation and polymerization processes in thin films are performed as easily as when cobalt naphthenate is used as a catalyst component.

When comparing the curves of photooxidative ageing it has been found that after little oxidation (for 5-7 days) leading to the appearance in IR-spectrum of absorption bands of oxygen-containing functional groups, the oxidation process is completely stopped (Figure 5).

Hence, the products of the catalytic dithiosystems oxidation are the most effective stabilizers of not only thermo-, but photooxidative ageing of PBD. On the other hand, the complete stop of the oxidation processes is evidenced by the availability of the catalytic inhibition effect under the action of the primary products of catalyst-stabilizers components (cobalt-containing catalytic dithiosystems).

It is known that the polymers stabilization consists in catalytic and free radical inhibition [21]. The pro-

Figure 5. IR-spectra of photooxidative pure PBD: 1- PBD pure, immediately after polymerization; 2,3,4-PBD after atmospheric ageing process in 2,4 and 7 days.
ceeding of these reactions may be facilitated by the presence of the transition metals compounds and especially, organo-aluminium compound. In interaction of cobalt dithioderivatives with alkyl aluminium halogenides the complexes containing bridged-bound dithiogroup are formed:

The phosphothione sulphur in these complexes seems to be more accessible for interaction with the hydroperoxide and peroxide radicals as a result of which the efficiency of the dithiosystems stabilizing action increases sharply. Recently there has appeared some information on the inhibiting effect of some Lewis acids on a radical-chain process of oxidation by molecular oxygen of the individual organic compounds [22]. The authors believe that the Lewis acids - compounds of elements of III, IV and V main groups of the Periodic system repeatedly participate in the reaction of chain rupture of oxidation, interact with peroxide radicals ROO•. In this connection, it might be thought that the high stabilizing efficiency of the catalytic dithiosystems in comparison with the starting cobalt dithioderivatives is due to not cobalt but aluminium component of the catalytic system, i.e. organoaluminium compound taken in large excess. It is, however, understood, that the high stabilizing efficiency of dithiosystems cannot be attributed to the contribution of the only alkyl aluminium chloride itself and it is due to just availability of dithiophosphate ligand in the catalytic system.

CONCLUSION

The systematical investigations of the catalytic and stabilizing properties of the dithiosystems on the basis of the cobalt organic dithioderivatives and alkylaluminium chlorides in the processes of 1,4-cis polybutadiene synthesis and stabilization enable us that on the basis of these compounds to create the bifunctional catalyst-stabilizers with simultaneously high catalytic and stabilizing effect.

The activity of the bifunctional catalyst-stabilizers is determined by the ligand surroundings in the starting complex of cobalt organic dithioderivatives and there is a similarity in the series of the catalytic activity and stabilizing effect. To reach the most effective combination of the catalytic and stabilizing properties of the cobalt-containing bifunctional catalysts for butadiene polymerization, it is necessary to introduce into the complex the ligands, containing, besides the dithiogroup, in addition the functional groups providing the synergistic effect in the polymer thermo- and photooxidative ageing.

It has been established that the products of the catalytic dithiosystems oxidative conversion as well as the cobalt organic dithioderivatives themselves, containing the oxyphenyl fragments, are more effective inhibitors of oxidation than the starting components.

By the efficiency of thermo- and photooxidative stabilizing action the cobalt-containing catalytic dithiosystems significantly surpass the commercial antioxidant Agidol (NG-2246) and this is explained by the effect of catalytic inhibition in the dithiosystems. In their combined use the good compatibility of two antioxidants and synergistic actions has been found.

ACKNOWLEDGEMENTS

Financial support of this work by the Institute of Petrochemical Processes Azerbaijan National Academy of Sciences, Baku, Azerbaijan Republic, is gratefully acknowledged. I thank Professor A.H. Azizov and Professor N.F. Janibeyov for helpful discussion, and also my coworkers of Laboratory “Technology of Metallocomplex Catalysis Processes” (Ms F.M. Novruzova, Dr. R.G. Hajiyev, and Dr. I.E. Jafarov). Finally my thanks to Mr R.K. Hasanov for the skilful typing of this manuscript.

SYMBOLS AND ABBREVIATIONS

PBD = polybutadiene
Co = cobalt
Ni = nickel
DTD = dithioderivatives
DEAC = diethylaluminiumchloride
DTPh = dithiophosphate
DTC = dithiocarbamate
X-Co = cobalt $O, O$-di-(3,5-di-tert-butyl-4-hydroxy-phenyl) di thiophosphate
CTPh-Co = cobalt $O, O$-di-4-methyl-phenyl di thiophosphate
4m-6-TBPh-Co = cobalt 2,2'-thio-bis-$O, O$-di-4-methyl-6-tert-butyl-phenyl di thiophosphate
DEDTC = $N, N$-diethyl dithiocarbamate
NGDTPh-Co = cobalt $O, O$-di-(2,2'-methylene-bis-4-methyl-6-tert-butyl-phenyl) di thiophosphate
DiPDTPh-Co = cobalt $O, O$-di-isopropyl dithiophosphate
DEDTPh-Co = cobalt $O, O$-diethyl dithiophosphate
IR = infra-red

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