PERSPECTIVE USING OF PHENOLIC COMPOUNDS WITH TRICYCLIC ADAMANTYL SUBSTITUENTS AS POLYMERISATION INHIBITORS IN THE PROCESSING OF LIQUID PYROLYSIS PRODUCTS

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Summary

Experimental results demonstrated that two phenolic compounds - 2,6-di-adamantyl-4-methylphenol and 2,4-di-adamantyl-6-methylphenol - are highly effective polymerisation inhibitors in the processing of liquid pyrolysis products (pyrocondensate). In laboratory conditions the two phenols showed very high inhibitory effectiveness in depressing the formation of polymer deposits which could be yielded from unsaturated components of pyrocondensate.

At concentrations of 0.01 - 0.05ppmw the inhibitory effect of 2,6-di-adamantyl-4-methylphenol and 2,4-di-adamantyl-6-methylphenol varied in the interval of 54 - 77% and 36 - 59%, respectively. In comparison to the effectiveness of industrial inhibitor 2,6-di-tertbutyl-4-methylphenol the figures of 2,6-di-adamantyl-4-methylphenol are about 1.7 times higher.

1. Introduction

Angarsk Polymer Plant (in Angarsk City, Russia Federation) provides plastic products and a wide range of monomer, such as ethylene, propylene for producing resins to the Russian market. Through around 40 years of its history, Angarsk Polymer Plant (APP) has always encountered one serious problem. In pyrocondensate processing, under high temperature olefins are usually polymerised and form polymer deposits which fall on the surface of pipeline equipment and decrease heat transfer, hammer plates of distillation columns and lessen the economic effectiveness of petrochemical plants [1].

In APP, practice has shown that the using of polymerisation inhibitors is the most selective and cost-effective way to deal with the undesirable formation of polymer deposits in pyrocondensate processing, in production, in storage and in transportation of monomers and fuels. The main role of inhibitors is to depress or/and reduce the rate of radical reaction of unsaturated compounds which usually occurs under high temperature. The assortment of compounds used as such specific additives is very wide. Because of their efficiency and adaptability, phenolic compounds are the most common polymerisation inhibitors used in processing unsaturated components of liquid pyrolysis products, especially in the Russian petrochemical plants [2].

Experience of APP's experts in using inhibitors over 30 years showed that the most widely-used and potent polymerisation inhibitors are sterically hindered phenols due to their high efficiency, low toxicity, high thermal stability and high antioxidant activity [2 - 4].

According to [5] phenols with the hydroxyl group shielded by large substituents have high solubility in organic solution and high anti-radical activity. For example, the above-mentioned properties of isobornylphenols (organic compounds with bicycle substituents) have been

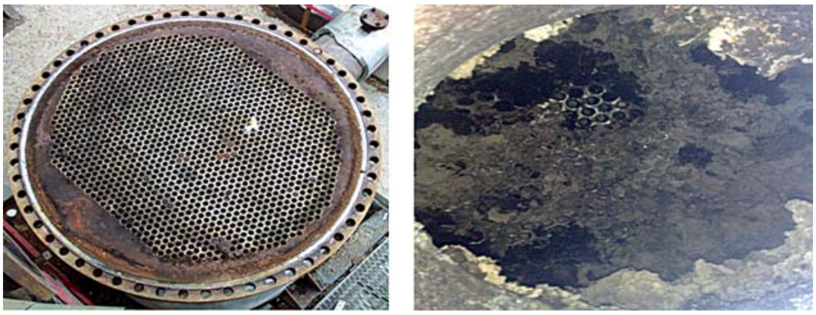


Fig.1. *The surface of fractionator's trays in the case of using highly effective phenolic inhibitor and uneffective nitroxyl radicals*

confirmed by the results of laboratory experiments in pyrocondensate processing [6] and also by the data of antiradical activity in reaction with stable 2,2-diphenyl-1-picrylhydrazyl radical (DPPH) [7].

The experimental data [7] showed that among isobornylphenols only compounds whose hydroxyl group on both sides is shielded by isobornyl substituents have the highest anti-radical and inhibitory activity. Furthermore, these properties depend significantly on the structure of phenols: on the number of large substituents and on the mutual positions of substituents in the molecule relative to the reactive centre (OH-group). So it is expected that phenolic compounds with larger (tricyclic) substituents could have higher inhibitory effectiveness. From this point, phenolic compounds with adamatyl substituents should be perspective candidates. It is important to be reminded that some good properties of adamatyl phenols, such as biological activity, thermal stability, and low toxicity, have already been shown in some papers [13, 14]. However, the activity of these substances in inhibiting polymerisation reactions which usually occur under high temperatures in the processing of liquid pyrolysis products has not yet been studied.

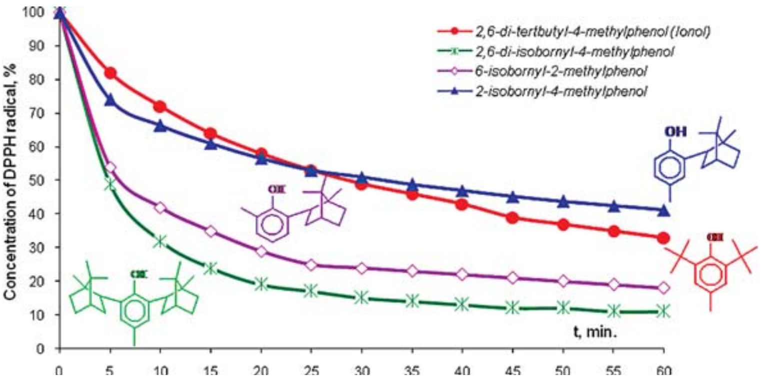


Fig.2. *Antiradical activity of isobornylphenols defined by the reaction with DPPH [7]*

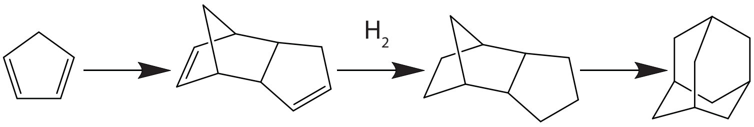


Fig.3. *Synthesis scheme of adamantane from cyclopentadiene*

In addition, it is well known that adamantane and its derivatives can be obtained at the petrochemical plants from its own materials - from cyclopentadiene-dicyclopentadiene (CPD-DCPD) fraction - by simple catalytic reactions [8]. For example, the industrial method for synthesis of adamantane from CPD has been studied and well organised (Fig.3) [9]. Various strong Lewis acids, such as $AlCl_3$ and $SbCl_3$ can be used as catalysts for this reaction. Moreover, the synthesis of adamantylphenols has now been fairly well mastered [10 - 12].

From the foregoing, the testing of inhibitory activity of adamantylphenols in pyrocondensate processing is essential and shows a certain scientific interest.

2. Experiment

2.1. Purpose of study

Evaluating the effectiveness of monohydroxy adamantylphenols in inhibiting formation of polymer deposits which occurs in pyrocondensate under high temperature; the experiment was carried out in a laboratory condition (130 ± 2°C) which was similar to the production condition of the Angarsk Polymer Plant (APP).

Table 1. *Essential unsaturated compounds of pyrocondensate K-20, wt. %*

Components	Quantity, % mass
2-methyl-butene-1	1.53
3-methyl-butene-1	0.32
2-methyl-butene-2	0.77
1-butyne	0.37
1,2-butadiene	0.12
1,3-*trans*-pentadiene	2.10
1,3-*cis*-pentadiene	1.67
1,4-*trans*-pentadiene	0.75
1-pentene	1.09
3-ethyl-pentene-1	6.45
4-methyl-pentene-2	0.46
cis-pentene-2	0.32
trans-pentene-2	0.60
isoprene	1.18
cyclopentene	1.37
3-ethyl-pentene-1	6.45
styrene	0.31

Table 2. *Distillation fractions of pyrocondensate which were determined on "АРН-ЛАБ-03"*

Temperature (°C) reaching after different amount (% vol.) of pyrocondensate K-20 was distilled										
Starting boiling point	10	20	30	40	50	60	70	80	90	97.5
44.0	56.0	60.5	66.0	70.5	74.0	81.0	85.5	97.5	147.5	173.0

2.2. Subjects of study

In this research, liquid hydrocarbon mixtures of fractionator N°-20 of the technological pipeline of APP (abbreviated as pyrocondensate K-20) were used as the objects for evaluating the inhibitory effectiveness of 2,6-di-adamantyl-4-methylphenol and 2,4-di-adamantyl-6-methylphenol.

Before each series of experiments the composition of pyrocondensate K-20 was studied by the Scientific and Research Centre (S&RC) of APP by chromatography mass spectrometry "Hewlett Packard-5MS" using the database of Angarsk Petrochemical Complex. The results are presented in Table 1.

The fractions of pyrocondensate K-20 were determined on the "АРН-ЛАБ-03" using the method of determining the fractions of the petroleum products (Table 2). In addition, some other properties of pyrocondensate K-20, provided by S&RC, are showed in Table 3.

2.3. Adamantylphenols used in this research

Phenolic compounds - adamantylphenols - used in this program were synthesised and provided by W.A. Sokolenko - senior researcher of the Institute of Chemistry and Chemical Technology, Siberian Branch of the Russian Academy of Sciences. These compounds are:

2,6-di-(1-adamantyl)-4-methylphenol (26DA4MP) (Fig.4a): synthesised by alkylation of p-cresol with 1-adamantanol at temperature 18 - 20°C in the presence of trifluoroacetic acid (TFA) as a catalyst [15]. 26DA4MP is white crystalline substances melting at 262 - 263°C.

2,4-di-(1-adamantyl)-6-methylphenol (24DA6MP) (Fig.4b): obtained by the reaction between o-cresol and 1-adamantanol in TFA catalyst [16]. This organic compound is a white crystal whose melting point is 245 - 247°C.

2.4. Methods of studying the inhibitory effectiveness of adamantylphenols

2.4.1. Evaluating the inhibitory effect of adamantylphenols using Budarov's method

By this method, the inhibitory effectiveness of adamantylphenols was determined by metering the inhibitor into an autoclave with pyrocondensate. Then, the autoclave with pyrocondensate and a certain amount of inhibitor experienced heat treatment at 130°C for 1 hour. Thence, the mixture was cooled to room temperature (~22°C), and the determination of polymer deposits formed after heating was carried out in appliance with the Russian GOST 8489-85 [17] on special device "ПОС-77М" (Fig.6).

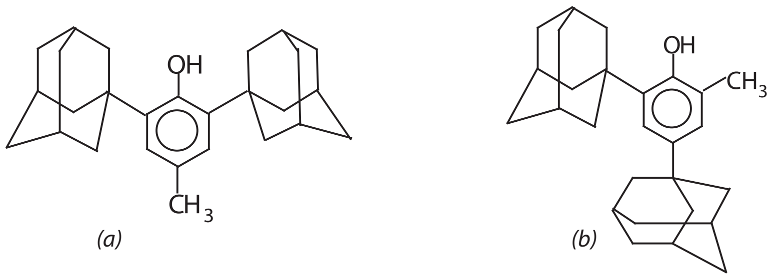
A typical experiment includes the following steps:

- 100ml pyrocondensate was poured into a stainless steel autoclave (a type of reactor working under high pressure), and then a certain amount of inhibitor in the range from 0.01 - 0.05wt. % in comparison to mass of pyrocondensate was added to the autoclave.

- Then, the autoclave was carefully sealed and put into an oil thermostat which was already preheated to 130 ± 2°C. The temperature was kept at this level for 1 hour, then the autoclave was taken out and cooled down to room temperature;

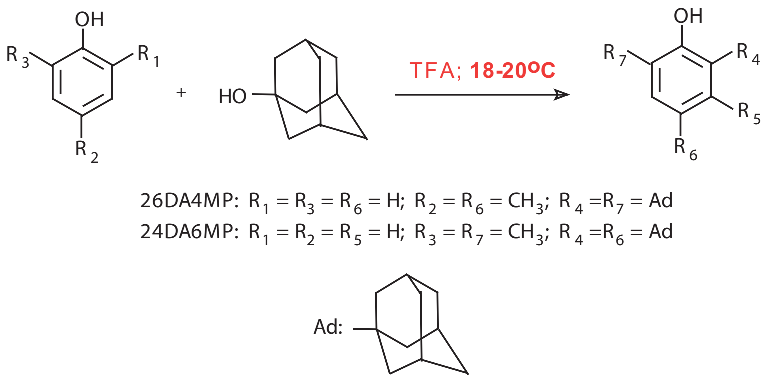
Table 3. *Other properties of pyrocondensate*

Properties	Pyrocondensate K-20
Iodine number, g I_2/100g pyrocondensate	92
Average molecular weight, g/mole	87
Fractional composition	Primarily fraction C_5-C_7



(a) (b)

Fig.4. *Structure of 2,6-di-(1-adamantyl)-4-methylphenol (a) and 2,4-di-(1-adamantyl)-6-methylphenol (b)*



26DA4MP: $R_1 = R_3 = R_6 = H$; $R_2 = R_6 = CH_3$; $R_4 = R_7 = Ad$
24DA6MP: $R_1 = R_2 = R_5 = H$; $R_3 = R_7 = CH_3$; $R_4 = R_6 = Ad$

Fig.5. *Synthesis scheme of 26DA4MP and 24DA6MP*

Fig.6. *Special device "ПОС-77M" used for determination of polymer deposits*

- In the next stage, pyrocondensate was distilled by water vapour at 160°C on the device type "ПОС-77M" and the polymer deposits were weighed (C_i);
- A parallel experiment without inhibitor was carried out, and then the quantity of polymer deposits was measured (C_0);
- Inhibitory effect of the inhibitor was determined by correlating the mass of the polymer deposits formed in the presence of the inhibitor with the mass of polymer deposits formed in the absence of the inhibitor. Inhibitory effect was calculated by the following formula:

$$E(\%)=\frac{C_o - C_i}{C_o}\times 100 \qquad (1)$$

The discrepancies between the results of two parallel experiments should not exceed the values given in Table 4.

Table 4. *Acceptable discrepancies between the results of two determinations*

Amount of polymer deposits, mg/100cm^3 of pyrocondensate	**Permissible differences**
Up to 15	2mg
Above 15 to 40	3mg
Above 40 to 100	8% of the lower result
Above 100	15% of the lower result

2.4.2. Determining inhibitory effect of adamantylphenols using the iodine number

The iodine number of pyrocondensate was determined by a standard method - the Russian GOST 2070-82 "Methods for determining the iodine number and concentration of unsaturated hydrocarbons" [18]. This method is widely used to determine the iodine number and the concentration (mass %) of unsaturated hydrocarbons in gasoline, diesel fuel and other light petroleum products.

The method is carried out by mixing alcoholic solution of iodine and pyrocondensate (gasoline, diesel fuel and other products). After that, the titration of the alcoholic solution with sodium thiosulfate solution ($Na_2S_2O_3$) is undertaken to determine the mass of free iodine (I_2) which did not react with unsaturated compounds in the pyrocondensate:

$$I_2 + 2Na_2S_2O_3 \rightarrow 2NaI + Na_2S_4O_6$$

Then the amount of iodine (g) involved in the reaction with unsaturated compounds containing in 100g pyrocondensate is evaluated.

Iodine number (Z) of pyrocondensate is calculated by the following formula:

$$Z=\frac{100\times(V_1-V_2)\times 0.012692\times F}{m} \qquad (2)$$

Where:

V_1 (cm^3): The amount of sodium thiosulfate consumed in the titration of iodine in a blank experiment (without pyrocondensate);

V_2 (cm^3): The amount of sodium thiosulfate consumed in the titration of iodine in the experiment with pyrocondensate;

F = 1: Factor of sodium thiosulfate solution 0.1mol/dm^3;

m: The mass of pyrocondensate;

0.012692: The amount of iodine contained in 1cm^3 solution of $Na_2S_2O_3$ 0.1N.

The iodine number of pyrocondensate is the average value of iodine numbers calculated from four parallel experiments, and then the iodine number is rounded to 1 decimal digit.

By the iodine number method, the inhibitory effect of the inhibitor is calculated using the following formula:

$$E(\%)=\frac{(Z_{130,(2)}-Z_{130,(1)})}{(Z_{20}-Z_{130,(1)})}\times 100 \qquad (3)$$

Where:

$Z_{130,(1)}$ and $Z_{130,(2)}$: Iodine number of pyrocondensate after heat treatment at 130°C in the blank experiment (without inhibitor) and in the experiment with inhibitor, respectively;

Z_{20}: Iodine number of pyrocondensate without inhibitor before heat treatment (20°C).

3. Experimental results and discussion

The data were determined by a series of experiments in laboratory conditions. The methods for determining inhibitory effects were introduced above (section 2.4).

Phenolic compounds with adamantyl substituents were thoroughly dissolved in pyrocondensate. Therefore, they can be dosed directly without using auxiliary solvents.

The experimental data showed that after heat treatment of pyrocondensate K-20 in the absence of inhibitor the level of polymer deposits was very high and reached 375mg/100cm^3 pyrocondensate. The figures decreased strongly to 206 - 262mg in the case of using ionol (Fig.7). It can be easily seen that in the presence of 26DA4MP the number dropped significantly to 85 - 171mg. This indicated that 26DA4MP was more effective than the widely used inhibitor ionol.

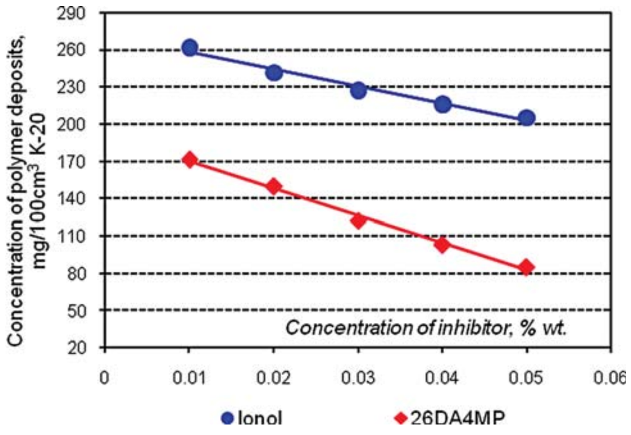


Fig.7. *Amount of polymer deposits formed in pyrocondensate K-20 at different concentration of 26DA4MP and Ionol*

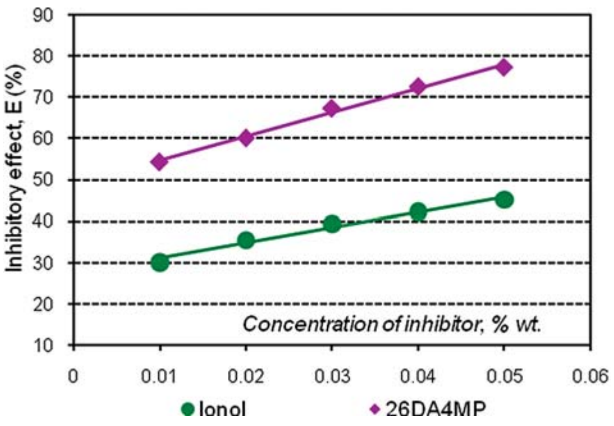


Fig.8. *Inhibitory effects of 26DA4MP and ionol*

Experimental results presented indicate that the compound 26DA4MP had high activity in inhibiting radical reactions of unsaturated components of pyrocondensate K-20. Indeed, on effectiveness, 26DA4MP far exceeds ionol - industrial inhibitor (Fig.8). In the range of inhibitor concentrations from 0.01 - 0.05 wt.% (or ppmw), inhibitory effectiveness of 26DA4MP reached 54 - 77% while the data of ionol gave the values of 30 - 45%. We can see that inhibitory effects of the two inhibitors increased proportional to their concentrations in pyrocondensate, and at any concentration the inhibitory effects of 26DA4MP were superior to the figures for ionol. It should be emphasised that at concentration 0.01wt.% the effectiveness of 26DA4MP reached 54% which was already higher than the data of ionol (45%) achieved at concentration 0.05wt.%.

We considered that the reasons for the higher inhibitory effectiveness of 26DA4MP in comparison to ionol are the following:

- First of all, 26DA4MP had higher solubility in pyrocondensate than ionol. At room temperature (~24°C) the average solubility of 26DA4MP in pyrocondensate is about 93mg/cm^3 while the number for ionol is only around 56mg/cm^3. Practice showed that if an inhibitor has good solubility in pyrocondensate (or in objects which need to be protected from polymer deposits formation) then the system "*inhibitor + pyrocondensate*" is more homogenous. Consequently, the inhibitory effectiveness of the inhibitor is high because the radical reactions between inhibitors and alkyl radicals usually are homogenous [20, 21].

- It is well-known that in depressing the formation of polymer deposits by using phenolic inhibitors the main process is the reaction of phenols (PhOH) or phenoxyl radicals (PhO•) with alkyl radicals:

$$PhOH + R\bullet \rightarrow PhO\bullet + RH \qquad (4)$$

$$PhO\bullet + R\bullet \rightarrow Ph_1O\bullet + R\bullet \qquad (5)$$

Unfortunately, some undesirable secondary reactions, such as reaction O-O-recombination of phenoxyl radicals usually occur parallel with the main reactions.

$$PhO\bullet + PhO\bullet \rightarrow Ph\text{-}O\text{-}O\text{-}Ph \qquad (6)$$

$$PhO\bullet + Ph_1O\bullet \rightarrow Ph\text{-}O\text{-}O\text{-}Ph_1 \qquad (7)$$

$$Ph_1O\bullet + Ph_1O\bullet \rightarrow Ph_1\text{-}O\text{-}O\text{-}Ph_1 \qquad (8)$$

However, the rate of reactions (6), (7) and (8) is high only if two ortho- positions from both sides of OH-group in phenols are small substituents. From this point, 26DA4MP was more effective than ionol because adamantyl groups are much larger than tert-butyl groups, so they prevented the contact of two phenoxyl radicals created from 26DA4MP. A possible schematic reaction O-O-recombination of phenoxyl radicals formed from phenolic inhibitors is presented in Fig.9.

From hypothetical schemes it could be understood that in pyrocondensate processing both directions (a) and (b) are not desirable because they lead to inefficient consumption of inhibitors. However, in the case of Ionol, direction (a) could occur because two *tert*-butyl substituents are not large enough to prevent the reaction O-O-recombination. On the other hand, reaction O-O-recombination (b) could not occur because two adamantyl chains are very large. Therefore, two phenoxyl radicals created from adamantyl phenol could not approach closely enough and react with each other.

The higher the rate of polymer deposits formation the lower the concentration of unsaturated compounds in pyrocondensate after heat treatment, and vice versa. In addition, the quantitative characteristic of the content of unsaturated hydrocarbons in pyrocondensate can be estimated by the iodine index of pyrocondensate.

It is clear that the higher the content of unsaturated compounds in pyrocondensate, the higher the iodine index of pyrocondensate. Based on this argument, iodine numbers of pyrocondensate before and after heat treatment in the case of using inhibitors and without inhibitors could be used as an independent method to assess inhibitory activity of ionol and 26DA4MP. The iodine values were calculated by formula (2) and presented in Table 5 and Fig.10.

The Fig.10 showed that at the concentrations in the range of 0.01 - 0.05%wt. in the case of using 26DA4MP as an inhibitor, iodine numbers of pyrocondensate reached the level of 63 - 76mg I_2/100mg pyrocondensate. When ionol is used the figures dropped to 50 - 58mg I_2/100mg pyrocondensate. In addition, it is clear that iodine numbers of both inhibitors were proportional to their concentrations in pyrocondensate.

By iodine number, the inhibitory effect can be calculated by formulation (3). The results are presented in Fig.11. As mentioned above, the higher the iodine index the higher the content of unsaturated compounds in pyrocondensate after heat treating under high temperature ~130°C, and consequently, the higher the inhibitory effect.

Based on inhibitory effectiveness determined by the two independent methods we can see that the inhibitor 26DA4MP was much more effective than industrial Ionol. Indeed, the inhibitory effects of 26DA4MP varied in the interval of 60 - 80% and about 1.63 times higher than the figures of ionol.

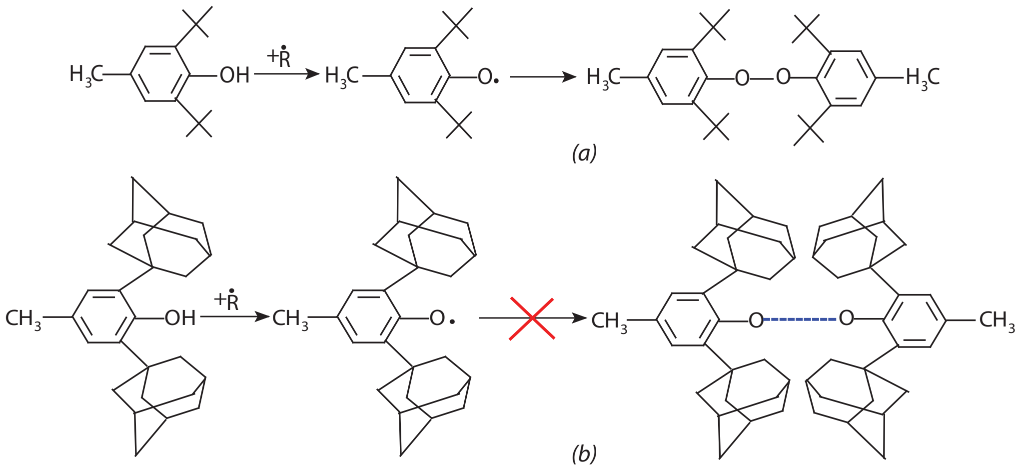


Fig.9. *Reaction O-O-recombination between phenoxyl radicals formed from ionol (a) and from 26DA4MP (b)*

Table 5. *Iodine number of pyrocondensate K-20*

		Temperature, °C	**Iodine number (Z) of pyrocondensate in case of using inhibitors at different concentration (% wt.)**				
			0.01	**0.02**	**0.03**	**0.04**	**0.05**
Inhibitor	WI *	20**	92.0				
		130***	30.8				
	Ionol	130***	50.4	54.1	54.3	58.5	57.9
	26DA4MP	130***	62.8	68.8	70.2	76.4	77.5

** - WI: Iodine number of pyrocondensate without inhibitor; **: Iodine number of pyrocondensate before heat treatment; ***: Iodine number of pyrocondensate after heat treatment at 130°C*

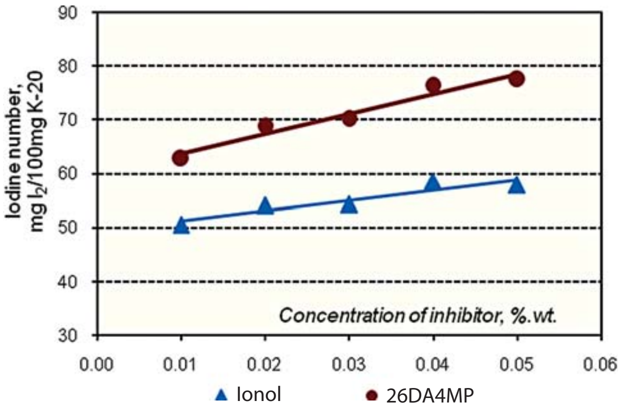


Fig.10. *Iodine number of pyrocondensate with inhibitor ionol or 26DA4MP*

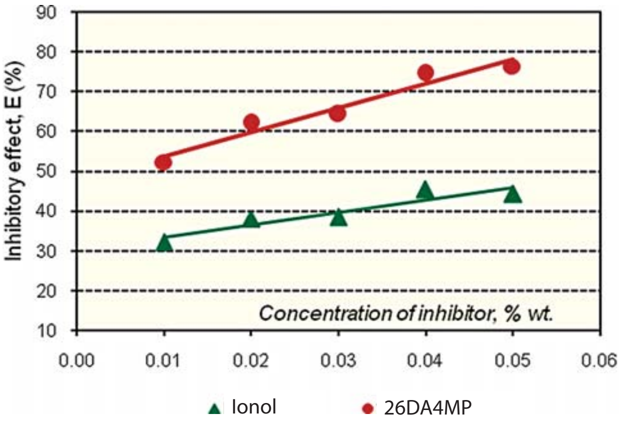


Fig.11. *Inhibitory effect of ionol and 26DA4MP evaluated by iondine number*

In comparison to 26DA4MP, its analogue - compound 24DA6MP - showed lower levels of inhibitory effect. However, this compound was still more effective than ionol.

The graph in Fig.12 shows that in the presence of 24DA6MP the quantity of polymer deposits achieved the level of 154 - 241g/100cm^3 pyrocondensate K-20. On the other hand, the data rose significantly to 206 - 262g/100cm^3 in the case of using ionol as inhibitor. This means that 24DA6MP was more effective in protecting unsaturated components from polymerisation reaction than ionol.

The experimental data (Fig.13) showed that at any concentration in the range of 0.01 - 0.05wt.% 24DA6MP's effects were higher than the figures for the industrial inhibitor - ionol. It was clearly seen that in the interval of 0.01 - 0.03wt.% the data of 24DA6MP increased from 35 - 58%. However, the figures remained stable at this level despite its concentration rising from 0.03 - 0.05wt.%. This indicates that a high concentration of 24DA6MP in pyrocondensate was not needed.

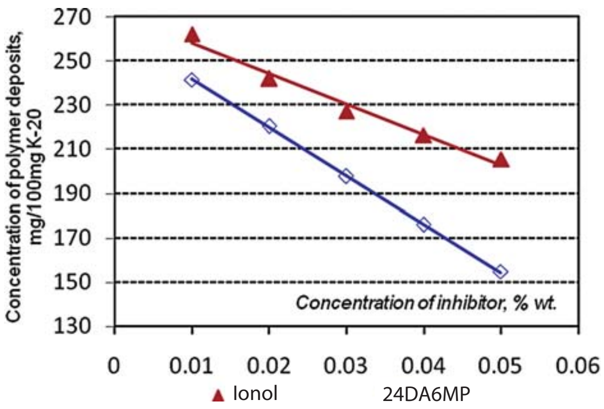


Fig.12. *Amount of polymer deposits formed in pyrocondensate K-20 at different concentration of 24DA6MP and Ionol*

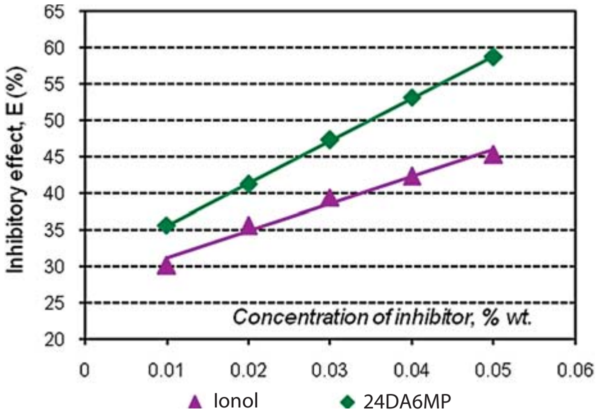


Fig.13. *Inhibitory effect of 24DA6MP and ionol*

It is supposed that at a high concentration of 24DA6MP, the unwanted O-O-recombination reaction of phenoxyl radicals (Fig.14) occurred more slowly than that presented in Fig.9a as the result of sterical effect of a large adamantyl group. However, the former could occur much faster than the O-O-recombination reaction showed in Fig.9b.

According to this scheme (Fig.14), phenoxyl radicals, which were formed from 24DA6MP, could rotate around its C-O axis and choose the most appropriate position to react with each other. Because of the small size of methyl group phenoxyl radicals formed from 24DA6MP, they were more active in participating in O-O-recombination reaction, and therefore, less effective in inhibiting the formation of polymer deposits.

It is very interesting that the change of relative positions of the methyl and adamantyl groups in the benzene rings (methyl group from para- position to ortho- position and adamantyl group from ortho- position to para- position) led to significant decrease of the inhibitory effect of phenolic compounds. This demonstrated that the sterical effect of large groups at ortho-positions (of benzene ring) is one of the key factors creating high inhibitory effectiveness of phenolic compounds.

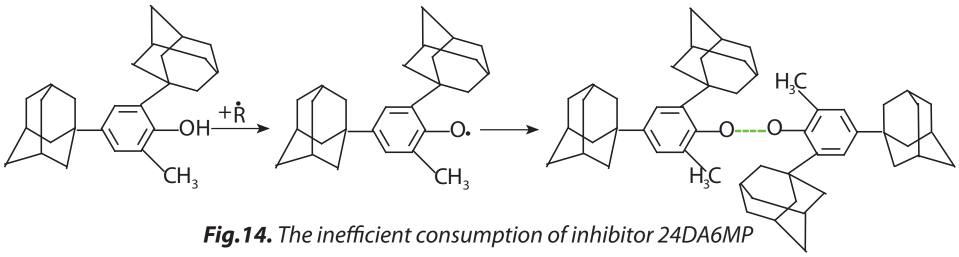


Fig.14. *The inefficient consumption of inhibitor 24DA6MP*

Table 6. *Iodine number of pyrocondensate K-20*

		Temperature, °C	Iodine number (Z) of pyrocondensate in case of using inhibitors at different concentration (% wt)				
			0.01	**0.02**	**0.03**	**0.04**	**0.05**
Inhibitor	WI *	20**	92.0				
		130***	30.8				
	Ionol	130***	50.4	53.4	54.3	58.0	58.3
	24DA6MP	130***	52.6	56.0	59.7	63.3	66.7

** : WI: Iodine number of pyrocondensate without inhibitor; **: Iodine number of pyrocondensate before heat treatment; ***: Iodine number of pyrocondensate after heat treatment at 130°C*

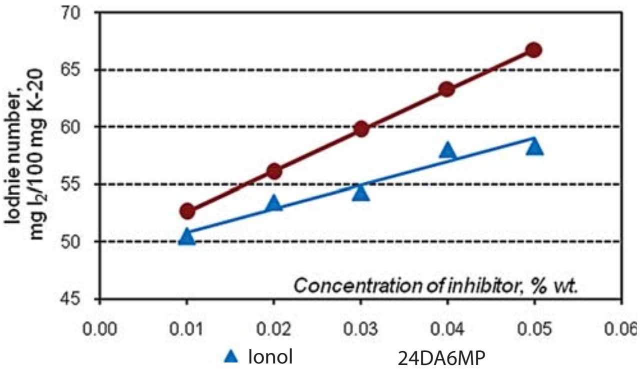


Fig.15. *Iodine number of pyrocondensate with inhibitor ionol or 24DA6MP*

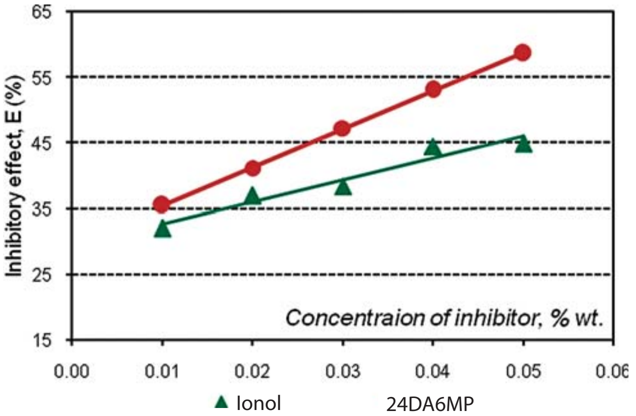


Fig.16. *Inhibitory effect of ionol and 24DA6MP evaluated by iondine number*

We also carried out the determination of the iodine index of pyrocondensate to study the inhibitory effectiveness of 24DA6M. The experimental figures are presented in Table 6 and Fig.15.

According to the experimental data, as the concentration of inhibitors varied from 0.01 - 0.05wt.% iodine numbers of 24DA6MP were higher than the figures of ionol by around 2 - 9 units. It means that 24DA6MP more effectively saved unsaturated components of pyrocondensate from polymerisation reaction than Ionol. Indeed, in the concentration range from 0.01 - 0.05wt.% the inhibitory effectiveness of ionol archived 32 - 45% while in this range of concentration the number of 24DA6MP increased from 36 - 59% (Fig.16).

4. Conclusions

The experimental results in laboratory conditions showed that two monohydroxy phenols with adamantly substituents at ortho- positions were highly effective polymerisation inhibitors in pyrocondensate processing. The inhibitory effect of 26DA4MP achieved 57 - 78% and is higher than that of ionol - widely used industrial polymerisation inhibitor - at around 19 - 20%. In addition, the study on the inhibitory effect of the two adamantylphenols has opened a new way of using phenolic compounds with tricyclic substituents as highly effective polymerisation inhibitors. It is considered that the use of adamantylphenols as inhibitors for processing of liquid pyrolysis products of Angarsk Polymer Plant is likely to bring high economic efficiency to the plant in the future. However, some testing of these compounds in an industrial scale trial is needed before using them in the plant's technological pipeline.

With the proven advantages on inhibitory effectiveness and, in addition, relatively simple synthesis and cheap source of raw materials, the use of these substances for petrochemical facilities, for manufacturing monomers, and for stabilising petroleum products in Vietnam is essential. However, in order to accurately assess the economic efficiency, some research on the specific products produced in Vietnam will be needed.

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