USE OF CHEMICAL BLOWING AGENT FOR FOAMING MODIFIED COAL TAR PITCH

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Coal tar pitch is a product of coal processing by high-temperature pyrolysis. Coal tar pitch has a set of properties that correspond to polymers. Due to the fact that coal tar pitch is a product of non-renewable natural resource, its use for obtaining high-tech and highly liquid products is relevant nowadays.

Pitch-based thermoplast is a completely new material. Coal tar pitch is subjected to low temperature modification by polymer additives at a temperature up to 180 °C for obtaining pitch-based thermoplast. The polymer additive was polyvinyl chloride (PVC). It's polar polymer with active functional groups.

The modified coal tar pitch (MCP) can be used as a polymer matrix to produce foamed pitch composites. The modified coal tar pitch is a product of low temperature modification of coal tar pitch by active polymers. It has a set of properties that correspond to amorphous polymers. The modified coal tar pitch has a viscosity from 55 to 190 Pa · s in the temperature range 125 – 155 °C [1]. Modified coal tar pitch is cheaper than classic polymers. It is characterized by chemical and biological stability and low thermal conductivity.

Many scientific papers are devoted to the obtaining a carbon foam based on coal tar pitch. The authors [2] proposed the use of strong oxidizing reagents such as H_2SO_4 to adjust the properties of the pitch and the formation of carbon foam based on this pitch. Other authors [3] proposed the high-temperature processing of the pitch and used it as a precursor to obtain a solid foam.

Our idea is to use the blowing agents to obtain a carbon foam at relatively low foaming temperatures. This is a fundamentally new method of obtaining the carbon foam.

The physical and chemical blowing agents are used for foaming the polymers. The physical blowing agents (PhBA) are used for obtaining polymeric foams based on polymers of low viscosity (up to 10 Pa · s).

The chemical blowing agents (ChBA) make the gas because of the chemical processes of thermal decomposition or due to various chemical reactions.

Azodicarbonamide ($NH_2CON=NCONH_2$) is the most common exothermic ChBA in the production of foam composites.

The decomposition temperature of azodicarbonamide (ADCA) is about 200 – 210 °C [6]. This temperature is too high to foam modified coal tar pitch because its rheological properties are changing [3]. The foaming process depends on the viscosity of the pitch polymer matrix. The pitch is in a highly elastic and viscous-flow state at temperatures of 130 – 150 °C. The pitch has a viscosity of 55 – 190 Pa · s. This viscosity ensures the formation of foams. The modified coal tar pitch shows the Newtonian liquid at temperatures above 195 °C, that means, it is a completely destroyed structure [3]. In addition, the pitch is subject to thermo-oxidative degradation.

The mechanism of ADCA decomposition are presented in Figure 1 [4]:

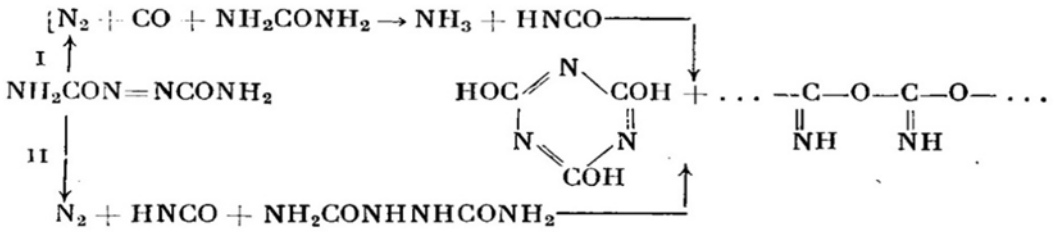

Figure 1. Scheme of the ADCA thermal decomposition

The ADCA thermal decomposition [4] consists of two stages: in the first stage (at temperatures of 180 – 220 °C) decomposition products are carbon monoxide, nitrogen and urea. In the second stage (220 – 320 °C) gaseous ammonia and solid isocyanic acid are formed. The material does not completely decompose into gaseous products. During the ADCA decomposition, 35% of gas, 40% of solid, and 25% of sublimate are formed. The gas consists of 65% nitrogen, 32% carbon monoxide and 3% other gases, including ammonia and carbon dioxide. Ammonia is formed, mainly at high temperatures.

It is known the decomposition temperature of ADCA can be reduced by activators (zinc and calcium salts). Some researchers believe [5], the salts of azodicarboxylic acid are formed when ADCA interacts with calcium or zinc salts. They are the activators of ADCA thermal decomposition.

During the research it has been proved that $ZnSt_2$ is the most active activator. The decomposition degree of the mixture ADCA-$ZnSt_2$ depends on the amount of activator $ZnSt_2$ and temperature. The mixture decomposition degree by $ZnSt_2$ increases when the temperature rises. The dependence of the decomposition degree from the activator amount is difficult and has an extremum at certain values of the activator amount. The amount of activator $ZnSt_2$ decreases with increasing temperature from 130 to 150 °C to achieve decomposition maximum degree.

Figure 2 shows the dependence of the complex blowing agent (ADCA-$ZnSt_2$) decomposition degree on temperature and the activator amount.

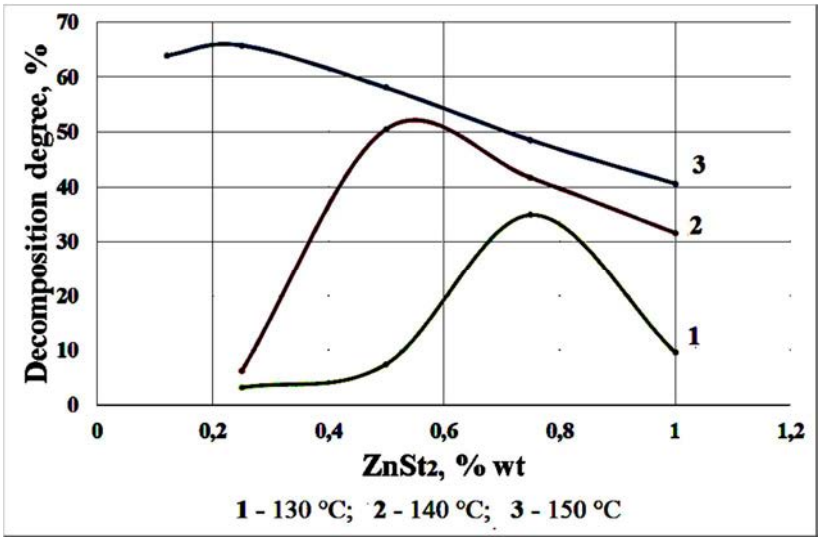

Figure 2. The dependence of the complex blowing agent (ADCA-$ZnSt_2$) decomposition degree on temperature and the activator amount

Figure 2 shows that for each temperature there is an extremum that corresponds to the decomposition maximum degree of the complex blowing agent ADCA-$ZnSt_2$. The amount of activator $ZnSt_2$ at each point of the maximum decreases with increasing the temperature. Therefore, there is a line of activator optimum amount to achieve the decomposition maximum degree of the the complex blowing agent ADCA-$ZnSt_2$ at T = 130 – 150 °C.

Based on experimental data the equations of the dependence of the activator $ZnSt_2$ optimum amount and the decomposition maximum degree of the complex blowing agent from temperature was obtained. The CBA optimal composition for the selected temperatures was calculated with the help of these equations.

The optimal composition of CBA: ADCA-$ZnSt_2$ at the temperature of 150 °C was used to foam modified coal tar pitch. The foaming temperature was 150 C, the holdup time - 60 minutes. The composition based on the modified pitch had the amount of PVC from 10 to 20 % by weight to the pitch and the amount of CBA from 1 to 5 % by weight to the modified pitch.

The foam criterion (K_{foam}) was used to evaluate the foaming efficiency of the modified pitch by complex blowing agent:

$$K_{foam} = \frac{V_{foam}}{V_0}$$

V_0 – volume of material before the foaming;

V_{foam} – volume of material during foaming.

The foaming process depends on both the amount of PVC in the modified pitch and the amount of CBA.

Study has shown (Fig. 3) that K_{foam} of the pitch modified by 10% of PVC with an increase of the CBA amount (from 1 to 5%) decreases from 2.5 to 1.5. On the contrary, criterion increases to 2.85 when the PVC amount is 15 % in a modified coal tar pitch. An increase of the CBA amount (PVC in the amount of 20%) leads first to increase K_{foam}, and then to reduce it.

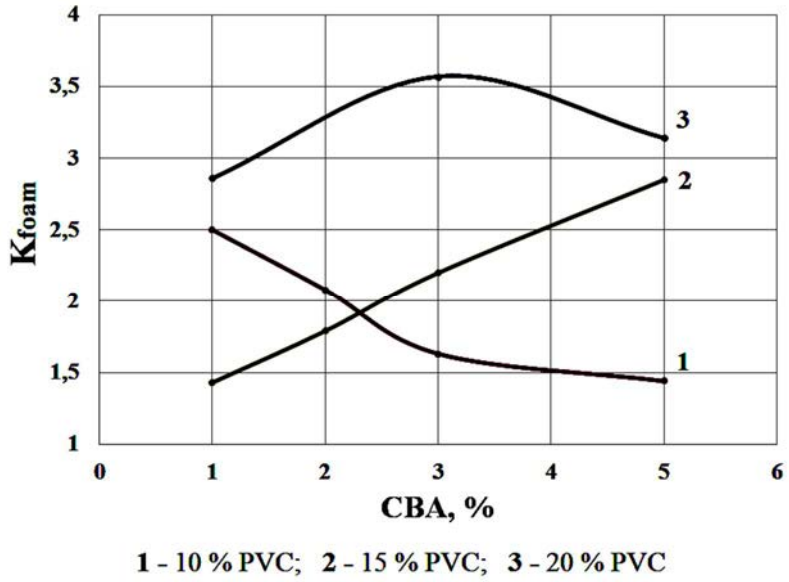

Figure 3. The dependence of the foam criterion (K_{foam}) from the CBA amount at T =150 °C and the holdup time of 60 minutes.

Figure 4 shows that K_{foam} for CBA 3% with an increase of the PVC amount (from 10 to 20 %) increases from 1.63 to 3.57. In the same time, criterion increases when the CBA amount is 5 % but the maximum value is only 3.14. An increase of the PVC amount (CBA in the amount of 1 %) leads first to decrease K_{foam}, and then to increase it. The maximum value of K_{foam} reaches 2.86.

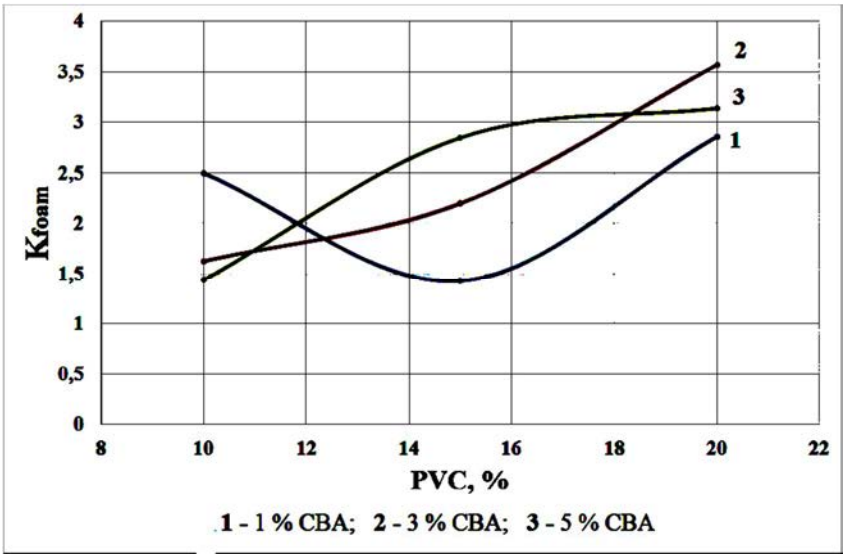

Figure 4. The dependence of the foam criterion (K_{foam}) from the PVC amount at T = 150 °C and the holdup time of 60 minutes.

During research, it was found that $ZnSt_2$ is the most active activator. The research has shown that the decomposition degree of the mixture ADCA-$ZnSt_2$ increases and the activator $ZnSt_2$ amount decreases to achieve the decomposition maximum degree with increasing the temperature. There is a line of optimal amount of $ZnSt_2$ for the complex blowing agent ADCA-$ZnSt_2$ to achieve the decomposition maximum degree at T = 130 – 150 °C. The decomposition maximum degree of the ADCA-$ZnSt_2$ mixture at an activator optimal amount is 65.8% at T = 150 °C.

The equations of the dependence of the activator $ZnSt_2$ optimum amount and the decomposition maximum degree of the complex blowing agent from temperature was obtained.

The maximum K_{foam} and the corresponding CBA amount for different composition of the modified coal tar pitch are determined. The highest foaming degree K_{foam} = 3.6 was achieved at the amount of PVC 20% and the amount of CBA 3%.

Experimental studies have shown that the selected CBA (ADCA-$ZnSt_2$) can be used for foaming MCP.

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