DEVELOMENT OF OZONE-DYNAMIC TECHNOLOGY FOR PROCESSING OF USED TYRES

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The results of research on the influence of different factors on disintegration of rubber goods by the ozone-dynamic method are presented. The dependence of disintegration rate on the time of treatment, temperature and humidity of gas in the chamber, ozone concentration and the activating chemical reagents were studied. This allows increasing efficiency of rubber goods processing by 30%. The dependence of the starting time for disintegration stages on ozone concentration in the chamber was determined. This allows optimizing the process of disintegration for rubber goods and gives the mechanism to control the process.

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INTRODUCTION

Annually more than 2 billion of used tires generated in the world and they should be utilized. Taking into account that tires are a multi component product and its composition includes rather expensive materials, the ideal method for tire processing, from the point of view utilization, is a separation of a tire in components (rubber, metal and textile) and subsequent individual processing of each component. Such approach with using mechanical grinding is the most popular today in the developed countries. Unfortunately, only 23% of used tires are treated in such way [1] due to high energy intensity of the treatment process which becomes economically feasible only for large processing capacitances (more than 2000 tons per year).

In the 90s, a new approach to the used tire treatment has begun to develop [2]. A well-known phenomenon of rubber cracking under the exposure in an ozone atmosphere was exploited for the used tire processing. Further research on the application of ozone-enriched gas for tire disintegration with subsequent separation of materials included in tire composition was fulfilled in [3]. As a result, the high rate of the tire disintegration was demonstrated. The amount of rubber crumb getting from the treated tire was 90…95% of total amount of rubber in tire. In addition, textile and metal cord with insignificant remaining rubber were obtained. It should be noted, that the obtained rubber crumb is completely free from metal and textile impurities, and also percentage of rubber powder with the size less than 1 mm is a very high for a single-stage process and makes 10…15% of total amount rubber crumb [4].

For further optimization of the ozone-dynamic technology for tire processing, the dynamics of rubber cracking was studied depending on ozone concentration, temperature and humidity of gas, activating chemical admixtures and etc.

EXPERIMENTAL STAND

The stand for conducting experimental research on tire disintegration was developed and built. The stand allows studying the dynamics of cracking forming for tire samples under different controlled conditions and as a result, the rate of disintegration, total weight and crumb rubber particle size distribution were studied.

The experimental stand is presented at Fig. 1 and includes the following components: 1 – oxygen generator ONYX+; 2 – gas flow meter; 3 – Stream Ozone ozone generation system; 4 – ozone monitor Mini-HiCon; 5 – chamber for tire sample treatment; 6 – hydraulic press.

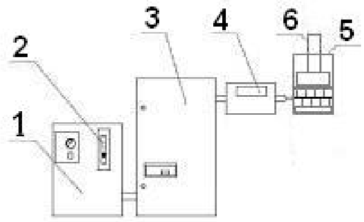

Fig. 1. Schematic of the experimental stand

Also, the working chamber was equipped with humidity meter IVTM-7 for control of humidity and temperature of gas during experiments.

To control the concentration of the different activating chemical admixtures during the fulfilled research on the combined action of the ozone environment and activating substances on the dynamics of tire sample disintegration, the chromatographic analysis of gas composition was carried out by using a gas chromatograph HP 5890 Series II with capillary chromatograph column Rtex-5 30m*0.53mmID*1.5um df.

Ozone for experimental research was generated by the ozone generation station «Stream Ozone» (Fig. 2) with the productivity of 12 g [O_3]/h. Maximal ozone concentration is of 60 g/m^3. The flowrate of ozone-enriched gas mixture changed from 0.06 to 0.6 m^3/h and was controlled by flow meter RM2-0.6 GUZ. Ozone concentration in the mixture changed within the range of 10…40 g/m^3 and was controlled using the ozone monitor Mini-HiCon with the accuracy of 0.1 gO_3/m^3.

Fig. 2. The ozone generation station «Stream Ozone»

As the chamber for ozone-dynamic disintegration of tire samples the metallic cylinder with the diameter of 170 mm and height of 400 mm was used. The module for application and distribution the dynamic mechanical impact on the tire sample has been mounted inside the cylinder. The mechanical load was applied using the hydraulic press JTC-HD210 with the maximum load of 10 tons. For the experiments, the tire samples were cut out from the protector part of the tire Voltyre Start VS-6 195/65 R15 91U. All the samples had the same size of 100×100 mm. The samples were put in between the movable and stationary flanges with the welded ribs that allowed creation of the undulating influence on the tire sample. The picture of tire sample in the module for the application of mechanical load is shown on Fig. 3.

a *b*

Fig. 3. Tire sample in the module for the application of mechanical load (a – before the disintegration process; b – after the disintegration process)

For studying the dynamics of crack forming in a tire under the desired ozone concentration and constant mechanical load, other type of chamber was used (Fig. 4).

Fig. 4. Experimental chamber with a transparent window

This chamber had a transparent window that allowed making photo and video for the tire disintegration process. It was the sealed chamber. The ozone-air mixture with the desired ozone concentration was pumped through the chamber. The volume of the chamber was 1.2 liter. The ability to apply only static load to the tire sample was in this chamber.

EXPERIMENTAL RESULTS

Rubber cracking under ozone-mechanical impact is a complicated physical and chemical phenomenon, in which the ozone initiates the rubber bonds breaking and if simultaneously tensile load is applied to rubber the broken bonds can not be bonded again. This results in crack formation. The cracks are developed while there is ozone and applied tensile load prevents the reverse bonding of the broken rubber bonds after oxidation by ozone of the double bonds with sulfur. Thus, the ozone-mechanical impact on the tire results in disintegration of tire structure and the crumbling of crumb rubber from the metal and textile carcass of a tire. The rate of tire disintegration or percentage of the crumb rubber output (α) can be determined as the ration of quantity of the obtained crumb rubber to the total weight of rubber in the tire. Usually the average amount of rubber makes 65…70% of the used tire weight, i.e. at the rate of disintegration 100% it can be obtained the different fractions of crumb rubber with the total weight of 65…70% from the initial weight of the tire. Residuals after treatment are the composite mix from a bead ring, textile and metal cord.

The researches on depending of rate of tire samples disintegration under the ozone-mechanical impact with different ozone concentration in gas mixture at the inlet into the experimental chamber were conducted. The following experimental parameters of gas mixture were used: gas flowrate – 0.2 m^3/h, ozone concentration at the inlet of the chamber was set in range from 1 to 30 g/m^3. Ozone was generated from the oxygen-enriched mixture with oxygen concentration of 92%. The temperature and gas humidity in the experimental chamber was controlled and kept a constant. The module for application the dynamic mechanical impact on the tire sample was used to provide the periodic reciprocating motion within the period of 3 minutes. The mechanical load in all experiments was applied in the same way. The time for tire sample treatment was 2 hours; it means that mechanical impact applied 40 times during the treatment.

The maximum ozone concentration in the chamber depends on the ozone concentration at the inlet in the chamber and on the kinetics of ozone decomposition at the surface of chamber construction and tire sample. The detailed description of this process is presented in article [5].

The experimental dependence of crumb rubber output on the ozone concentration in the gas mixture at the constant treatment time is shown on Fig. 5.

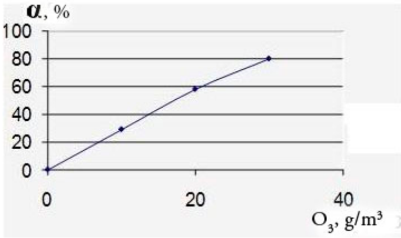

Fig. 5. Dependence of the rate of the tire disintegration on the ozone concentration at the constant treatment time of 2 hours

The results at Fig. 5 show that the crumb rubber output grows practically linearly with the growth of ozone concentration in the gas mixture. After exceeding the ozone concentration 20 g/m^3, the rate of disintegration slightly slows down due to the increasing of the ozone decomposition rate on both the structural parts of the working chamber and on the tire sample.

The dependence of the crumb rubber output on the treatment time at the constant ozone concentration (20 g/m^3) is shown on Fig. 6.

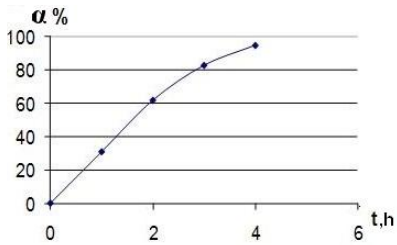

Fig. 6. The rate of tire sample disintegration vs the time of treatment. Ozone concentration is 20 g/m^3

The experimental data at Fig. 6 show that at the constant ozone concentration 20 g/m^3 if the treatment time for the tire sample is increased, the rate of rubber disintegration also is increased. At the beginning stage of treatment (under experimental conditions it is 2 hours), the rate of disintegration grows linear, and then the rate of the rubber disintegration decreases. A conclusion can be made, that the tire treatment time should be matched with the desired rate of tire disintegration and a specific power consumption to produce a crumb rubber.

Next the influence of temperature on the rate of rubber disintegration was studied. The experiments were carried out under the constant ozone concentration at the inlet in the chamber of 20 g/m^3 and constant relative humidity of gas in the chamber of 25%. Time of treatment is 2 hours. The experimental data are presented in table below.

№ s/p	$[O_3]$, g/m^3	Time t, hours	Temperature T, ^{0}C	Rate of rubber disintegration α, %
1.	20	2	25	62
2.	20	2	35	74
3.	20	2	45	67
4.	20	2	55	65

The maximal rate of the tire sample disintegration was achieved for a temperature in the working chamber of 35^{0}C. The subsequent increasing of temperature in the working chamber results in the decreasing the rate of the rubber disintegration due to acceleration of ozone decay in the gas mixture. Under temperature below 35^{0}C the rubber disintegration in the ozone-dynamic method is running slowly.

The influence of gas humidity in the working chamber was also studied. The humidity (and the moisture content, correspondingly) was changed at the controlled temperature by injection of the required quantity of water steam to the working volume of the chamber. Humidity was measured by the humidity meter IVTM-7.

The experimental results on the influence of humidity on the rate of rubber disintegration at the constant temperature of 25^{0}C and ozone concentration of 20 g/m^3 are presented in Fig. 7. Time of treatment is 2 hours.

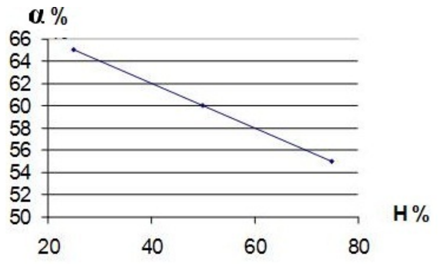

Fig. 7. Dependence of the crumb rubber output on humidity of gas in the chamber. Temperature is 25^{0}Cand ozone concentration is 20 g/m^3. Time of treatment is 2 hours

The presented experimental data show that as the moisture content grows in the working chamber, the output of crumb rubber from the tire sample decreases. It is explained by two effects. First, the increase of moisture content in the working chamber results in the formation of water film on the surface of tire which prevents ozone penetration to the internal layer of the tire. Second, the increase of water content in gas of the working chamber results in the increase the rate of ozone decomposition because the water molecules are an additional channel for reaction with ozone.

The activating chemical admixtures also can make the influence on rate of rubber disintegration. To study the rate of rubber disintegration for the tire samples depending on the level of chemical substances in gas of the working chamber, the only chemically pure substances were used, so that the presence of admixtures of other substances did not change the process dynamics. The solvents of benzol group (from benzol to isooctane) and ethyl acetate (containing oxide group) were selected as activating chemical substances. The concentration of chemical substances in the volume was 5 ml/l.

The histogram showing the change in the crumb rubber output for different activating chemical substances in the gas of the working chamber at the constant temperature of 25 ^{0}C and ozone concentration of 20 g/m^3 is presented in Fig. 8. Time of treatment is 2 hours.

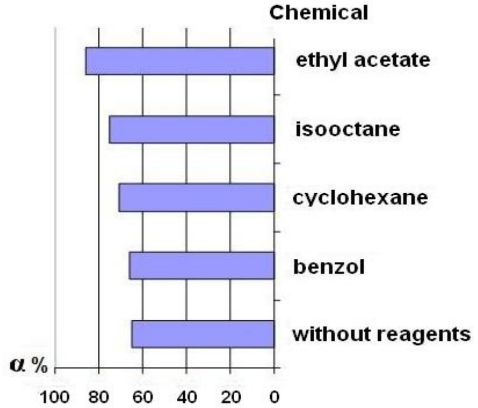

Fig. 8. The crumb rubber output for the different activating chemical substances in the working chamber. Temperature is 25^{0}C and ozone concentration is 20 g/m^3. Time of treatment is 2 hours

The experimental results show that the input of hydrocarbons to the working volume of the chamber allows increasing the crumb rubber output due to the initial softening of the tire surface that provides more effective penetration of ozone into the internal layers of rubber. Within the range of chemical substances from benzol (C_6H_6) to isooctane (C_8H_{18}), their oxidizing power decreases, that results in reduction of ozone losses for the reaction of oxidation with these substances. Ethyl acetate (CH_3-COO-CH_2-CH_3), as the chemical substance, contains an oxide group that decreases the rate of reaction for interaction with ozone and not only contributes to the softening of rubber surface, but also allows ethyl acetate to be the oxidant simultaneously with ozone.

To control the process of rubber disintegration, the experimental research on the dependence of time when the stages of disintegration appear on different factors were carried out. Using photo and video registration allowed specifying the characteristic stages of rubber disintegration process. The rubber crack formation under the influence of ozone is caused by oxidation of sulphur which is a vulcanizate. The development of cracks under given ozone concentration is taken place due to the mechanical load applying to rubber body to prevent the reverse bonding of the active bonds of polymeric molecules. Due to video registration it was determined that the tire disintegration process can be divided into 6 stages, presented in Fig. 9: 1 – formation of small cracks, 2 – junction of small cracks, 3 – appearance of big cracks, 4 – crumbling of the first crumb rubber, 5 – junction of big cracks, 6 – propagation the big cracks to the cord.

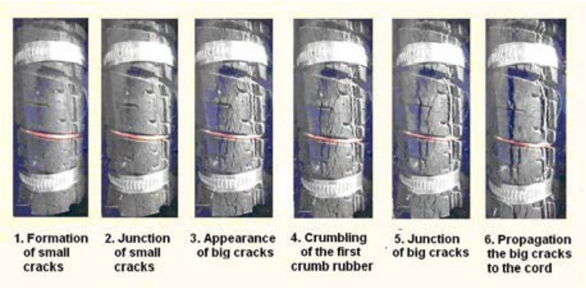

Fig. 9. Stages of tire disintegration

In accordance with the experimental results, the dependence of time for different rubber disintegration stages on ozone concentration in the chamber with the linear scale for y-axes was built (Fig. 10). The experiments were carried out with ozone concentrations in the gas mixture of 1, 5, 10, 20 and 30 g/m^3.

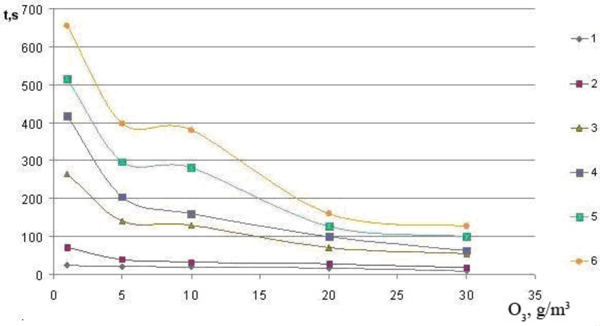

Fig. 10. The dependence of time for tire disintegration stages on ozone concentration in the chamber

In accordance with the equation presented below, the approximating lines are calculated and presented in the graphs with the logarithmic scale for y-axes (Fig. 11).

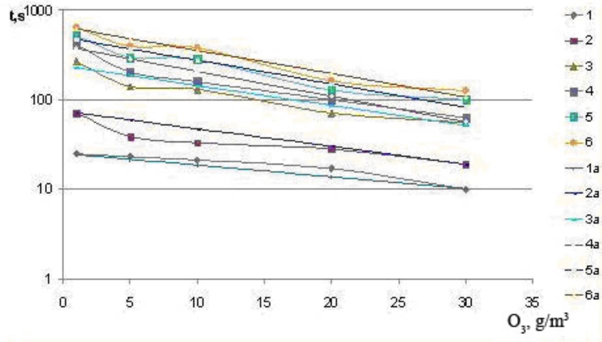

Fig. 11. The dependence of time for tire disintegration stages on ozone concentration in the chamber with the logarithmic scale for y-axes

$$T([O_3]) = T_0 \times K \times \exp(-\beta \times [O_3]),$$

where T_o – time of the beginning of the disintegration stage of starts at the minimum ozone concentration; K – constant depending on the stage of disintegration; β – angle of approximating line slope; [O_3] – ozone concentration in mixture.

The experimental data show that in the logarithmic scale the change of time for the rubber destruction stages in the experimental chamber is almost straight within a very wide range of ozone concentration change, that corresponds to the exponential character of dependence of time for the stages on ozone concentration.

CONCLUSIONS

The following conclusions can be made:

As a result of the fulfilled extensive research on the influence of different factors on disintegration of tire samples by the ozone-dynamic method, the dependence of disintegration rate on the time of treatment, temperature and humidity of gas in the chamber, ozone concentration and pactivating chemical reagents in the working gas is determined. This allows increasing efficiency of the tire disintegration at 30%. The dependence of time for the beginning of rubber disintegration stages on ozone concentration in the chamber was determined. This allows optimization of the rubber disintegration process and gives the mechanism to control the process.

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УСОВЕРШЕНСТВОВАНИЕ ОЗОНО-ДИНАМИЧЕСКОЙ ТЕХНОЛОГИИ ПЕРЕРАБОТКИ РЕЗИНОТЕХНИЧЕСКИХ ИЗДЕЛИЙ

В.И. Голота, Г.В. Таран, А.А. Замуриев

Приведены результаты исследований влияния различных факторов на дезинтеграцию резинотехнических изделий озоно-динамическим методом. Определены зависимости степени дезинтеграции от времени воздействия, температуры и влажности газа в камере, концентрации озона и наличия химических реагентов в составе рабочего газа. Это позволило повысить эффективность процесса переработки резинотехнических изделий почти на 30%. Определена зависимость времени начала наступления этапов дезинтеграции резинотехнических изделий от концентрации озона в камере. Это позволит оптимизировать процесс дезинтеграции резины и даст возможность управлять процессом.

УДОСКОНАЛЕННЯ ОЗОНО-ДИНАМІЧНОЇ ТЕХНОЛОГІЇ ПЕРЕРОБКИ ГУМОТЕХНІЧНИХ ВИРОБІВ

В.І. Голота, Г.В. Таран, О.О. Замурієв

Приведено результати досліджень впливу різних чинників на дезинтеграцію гумотехнічних виробів озоно-динамічним методом. Визначена залежність ступеня дезинтеграції від часу дії, температури та вологості газу в камері, концентрації озону і наявності хімічних реагентів у складі робочого газу. Це дозволило підвищити ефективність процесу переробки гумотехнічних виробів майже на 30%. Визначена залежність часу початку настання етапів дезинтеграції гумотехнічних виробів від концентрації озону в камері. Це дозволить оптимізувати процес дезинтеграції гуми і дасть можливість управляти процесом.