The Influence of Catalysts Addition on Blown Bitumens Characteristics

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The main method of road bitumen properties improvement consists in catalytic oxidation. In the paper are shown the results obtained in the oxidation of mass-asphalt in a discontinuous mixing device, for road bitumen. Catalytic systems used in oxidation process were iron nanoparticle, iron carboxylate and aluminum chloride. Oxidation efficiency was evaluated by determining the main characteristics of road bitumen (penetration, softening point, ductility, Fraass breaking point, asfaltene content and characteristics of aging). Making this process in the presence of catalysts favours the reduction the term of oxidation in the manufacture of bitumen by blowing air. Catalyst of type iron nanoparticles shows a higher efficiency than the type of iron carboxylate (as such or in the presence of aluminum chloride) in the oxidation process.

Keywords: blown bitumen, softening point, ductibility, penetration

Bitumen is a colloidal system that contains asphaltenes dispersed in malthenes. Colloidal particle size depends on the nature of raw materials and manufacturing mode [1]. Keeping the asphaltene particles in suspension is made by resins, so repulsive forces acting between the dissolved resin particles and adsorbed on the asphaltenes on the surface, prevent structures flocculation of associated asphaltene. Stability of such a colloidal system is determined by the following factors: the concentration of resins in solution, the proportion of asphaltene area occupied with resins molecules and the equilibrium conditions between resin in solution and those on the asphaltene surface. Reducing the resin content to a level that does not ensure full coverage of asphaltene surface at a constant content of asphaltenes and saturated and aromatic components, can contribute to irreversible aggregation of asphaltene particles, leading to their flocculation [2].

Bitumen composition is influenced primarily by the production technology, so the changes taking place in the composition of bitumen, as a result of blowing air during the production process depend on the type of crude oil that was used. Fractionation of asphaltenes showed a larger amount of asphaltene with higher molecular weight in heavy bitumens, which were blown with air. Analysis by GPC method confirmed a higher content of heavier elements in these bitumens. Chemical composition of raw materials and production technology for bitumen shows a great influence on the size of small asphaltene and the degree of aggregation [2].

Comparison between air-blown bitumens and those treated with acid shows that for both cases appears to shift from the structure of colloidal soil to gel. Gel structure ensures a good behaviour in terms of permanent deformation at high temperatures, and affect positive storage stability. Despite their common effect on the colloidal structure of bitumen obtained by blowing air and through the addition of polyphosphoric acid, the two methods differently affect low temperature performance, so the bitumen obtained by blowing air increases fragility, while chemical treatment does not change Fraass breaking point. Characteristics of sol-gel bitumens seem to significantly affect their performance in road applications [3].

Thermogravimetric analysis of a nigerian bitumen showed that thermal decomposition in air presentations resulting in three different reaction zones, namely oxidation at low temperatures, condensation and oxidation processes at high temperature. Heating rate variation resulted in a shift reaction zone to higher temperatures. The gas flow has no adverse effect on reactions [4].

The literature highlights various chemical and physical procedures to activate the raw material in bitumen production. The chemical activation means alternating chemical groups in order to change the chemical composition of the dispersion medium by introducing special chemical additives (extracted from the selective purification of oils, sulfur black oil, etc.) or removal of certain components that changes the average power of dispersion and particle size of the dispersed phase [5]. It was put into evidence that components like residue from oleic acid distillation, aromatic oil, and linseed oil, exhibit similar effects on the bitumen properties. Thus, by an adequate choice of their concentrations, the characteristics of modified bitumen could be optimized. The oxidized bitumen was evaluated by colloidal instability value, penetration, “ring and ball” softening point and ductility [6].

Getting bitumen by the classic blow air oxidation adversely affect the physico-chemical properties due to different reactivity in oxidation process of the main classes of chemical compounds present in raw materials. Thus, the specific working conditions of bitumen oxidation, branched or cyclic saturated hydrocarbons have a much lower reactivity towards oxidation of petroleum resin grades, asphaltene and aromatic hydrocarbons. This different behaviour favours changing the composition towards rising bitumen content at the expense of asphaltene petroleum resins and aromatic hydrocarbons,

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affecting the stability of colloidal pitch. This aging trend is accentuated due to increased asphaltene content.

These shortcomings can be overcome by using efficient catalysts that promote oxidation of all classes of chemical compounds present in bitumen, decreasing molecular weight of compounds produced and reaction time.

Experimental part

The raw material used in the experiments was an asphalt mass whose characteristics are presented in Figures 2-9 (code MP). Catalytic oxidation systems used for mass-asphalt are:

- iron-based nanoparticles;
- iron carboxylate (iron content: 6%);
- iron carboxylate + anhydrous aluminum chloride.

Iron-based nanoparticles (magnetite nanoparticles) were prepared according to modified Massart method:

- dosed under stirring (800rpm), a solution of ammonia to a mixture of $FeCl_2$ and $FeCl_3$ at 70 °C temperature;
- nanoparticles obtained were washed with distilled water and then dried.

Bitumen oxidation was performed in batch in a cylindrical reactor equipped with an electric heating system with automatic temperature range. Air circulation in the reactor is upward, dispersing the gas bubbles being achieved through a sieve. For all catalytic systems oxidation process was completed in the following values of parameters: air speed volume 40 h^{-1}, temperature 180° C. Oxidation duration, type and concentration of catalysts are listed in table 1.

Bitumen characterization was done by determining the following characteristics, namely: the penetration at 25^{0}C, softening point, ductility at 25^{0}C, Fraass breaking point, the aging-stability RTFOT (residual penetration, residual ductility, softening point increase), viscosity at 135^{0}C, asphaltene content and adhesion to the mineral aggregate.

Results and discussions

Iron nanoparticle size distribution was determined with a measurement system of particles dimensions by dynamic light scattering (Zetasizer Nano –Malvern Instruments) shown in figure 1. It shows a unimodal distribution with average particle size 102.4 nm and minimum particle size 36 nm.

Influence of oxidation catalyst on the asphaltene content of bitumen obtained is shown in figure 2. Asphaltene content of bitumen obtained grows more pronounced when using catalyst of iron nanoparticles type rather than using iron catalyst of iron carboxylate type or non catalytic oxidation. Thus asphaltene content of bitumen obtained by oxidation has increased by 60% compared to the raw material. A concentration of asphaltene appropriated to that resulting from oxidation of iron nanoparticles was obtained from oxidation with iron carboxylate in the presence of aluminum chloride in an oxidation period of almost three times higher. The presence of hydrophobic surfactant nonylphenol ethoxylate (NF 4) at a concentration of 0.3% decreases asphaltene content by about 6% in case of oxidation catalyst based on iron nanoparticles.

Influence of oxidation catalyst on penetration bitumen obtained is shown in figure 3. Penetration decrease is more evident in bitumen obtained by oxidation of iron nanoparticles than in bitumen oxidized with iron carboxylate or catalyst absence, at the same reaction time. Decreased penetration is lower if the dispersion of iron nanoparticles in hydrophobic surfactant NF8. Increasing the duration of the oxidation process reduces the penetration of nearly three times more than half, and the presence of aluminum chloride penetration reduces by almost half, for the same operating conditions.

Table 1
OPERATION PARAMETERS USED IN OXIDATION PROCESS

Sample cod	Description	Oxidationduration, h
MP	Raw material (asfalt mass)	-
BN1	Bitumen obtained through oxidation with Fe nanoparticules 0.3% dispersed in mineral oil	4
BN2	Bitumen obtained through oxidation with Fe nanoparticules 0.13% dispersed in nonylphenol (NF8) 0.3%	4
BC1	Bitumen obtained through oxidation without catalysts	4
BC2	Bitumen obtained through oxidation with 0.3% $_w$ carboxylate Fe	4
BC3	Bitumen obtained through oxidation with 0.3%$_w$ Fe carboxylate + 0.03% $AlCl_3$ anh.	4
BC4	Bitumen obtained through oxidation with 0.3%$_w$ Fe carboxylate + 0.03% $AlCl_3$ anh.	11

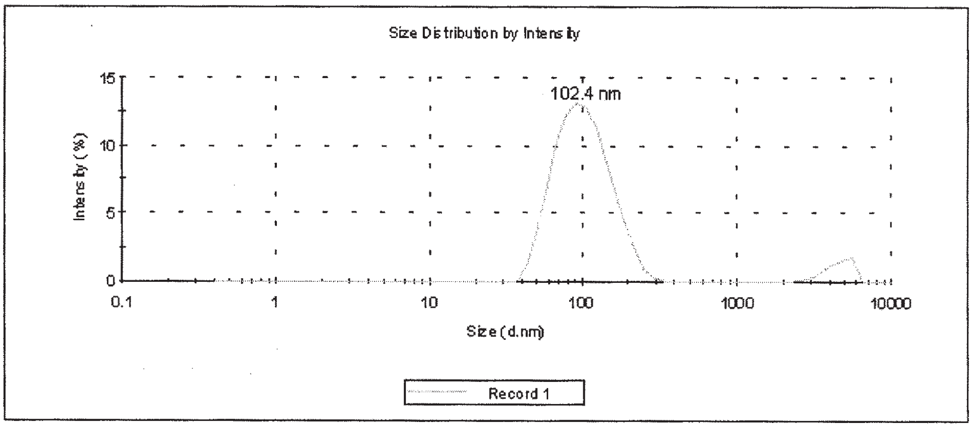

Fig. 1. Size distribution of iron nanoparticles

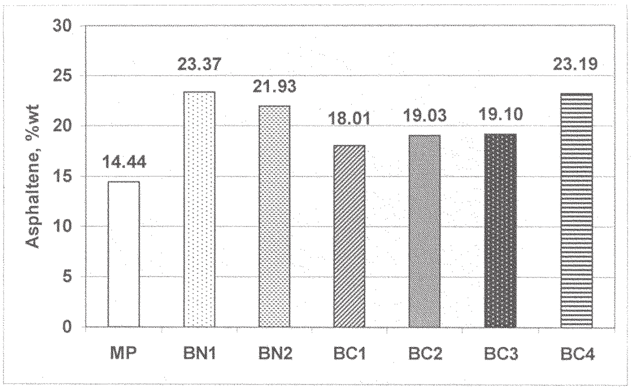

Fig. 2. Influence of oxidation catalyst on the asphaltene content of bitumen obtained

Influence of oxidation catalyst on the softening point of bitumen obtained is shown in figure 4. Increasing the softening point is more obvious at the bitumen obtained by oxidation of iron nanoparticles rather than in bitumen oxidized with iron carboxylate or in the absence of catalyst, reaction at the same time. Increasing the softening point is lower in case of the dispersion of iron nanoparticles in hydrophobic surfactant NF8. Increasing the process of oxidation by almost three times the growth-inducing softening point by 35%, and the presence of aluminum chloride softening point increases by about 15% for the same operating conditions.

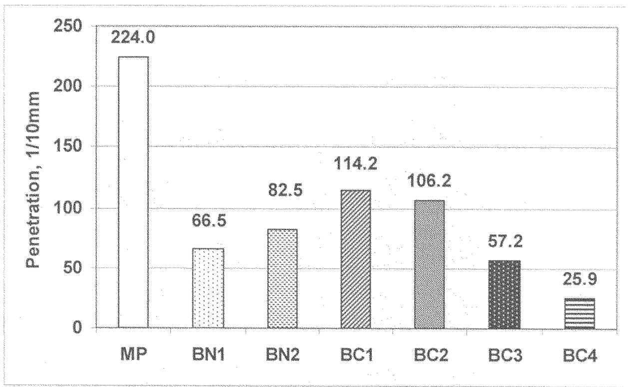

Fig. 3. Oxidation catalyst influence on penetration bitumen obtained

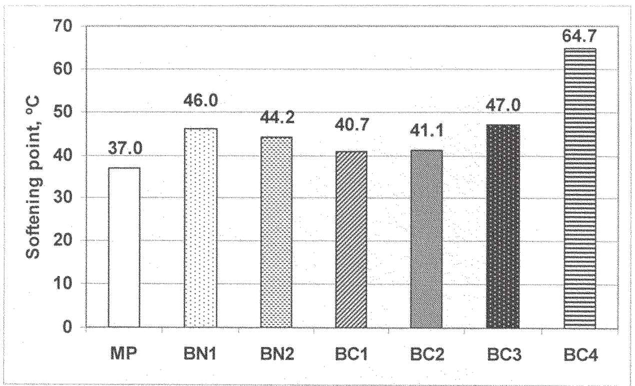

Fig. 4. Influence of oxidation catalyst on the softening point of obtained bitumen

Influence of oxidation catalyst on Frass breaking point of bitumen obtained is shown in figure 5. Frass breaking point changes insignificantly in bitumen obtained by oxidation of iron nanoparticles to the mass of the initial asphalt. Falling Frass breaking point drop is more pronounced in case of the dispersion of iron nanoparticles in hydrophobic surfactant NF8. Increasing the process of oxidation by almost three times Frass breaking point lead

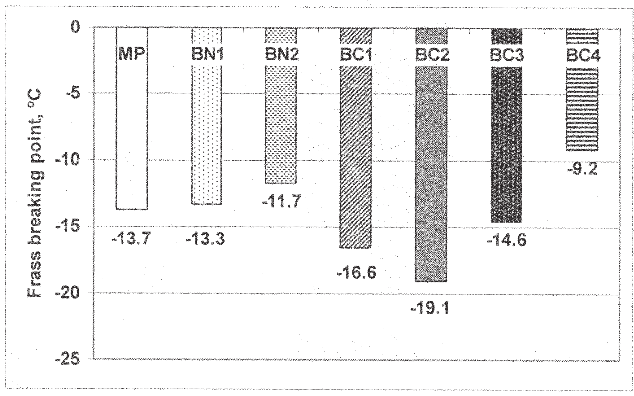

Fig. 5. Influence of oxidation catalyst on Fraass breaking point of the obtained bitumen

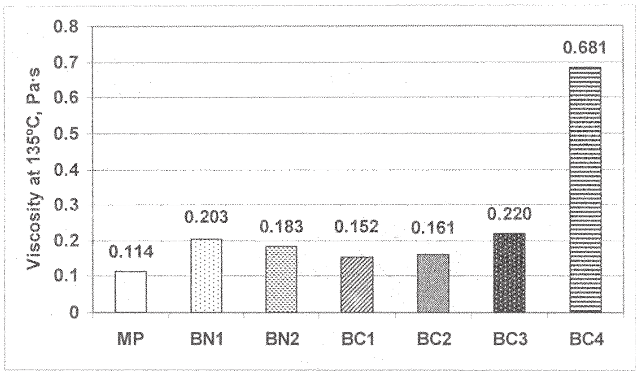

Fig. 6. Influence of oxidation catalyst on the viscosity of the obtained bitumen

by 35%, and the presence of aluminum chloride determines increases Frass breaking point by almost 20% for the same operating conditions.

Influence of oxidation catalyst on the viscosity of bitumen obtained at a temperature of 135^0 C is shown in figure 6. Increasing the process of oxidation by almost three times the viscosity enhance growth of almost 6 times in the same working conditions. Increased viscosity is more obvious at the bitumen obtained by oxidation of iron nanoparticles than in bitumen oxidized with iron carboxylate or catalyst absence, reaction at the same time. Increased viscosity is smaller in the dispersion of iron nanoparticles in nonylphenol ethoxylate (NF8). The presence of aluminum chloride viscosity increases by 35% for the same operating conditions.

Aging characteristics were evaluated by RTFOT method and are presented in figures 7-10. Residual penetration bitumen obtained by oxidation, expressed as a percentage of the initial one, is shown in figure 7. It shows a smaller variation of penetration with increasing duration of oxidation, also decreased penetration is more diminished

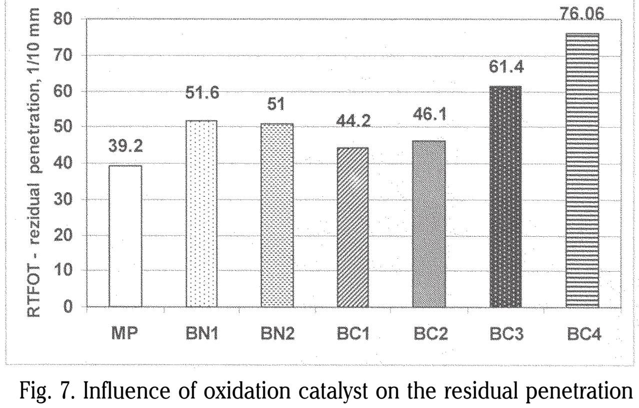

Fig. 7. Influence of oxidation catalyst on the residual penetration

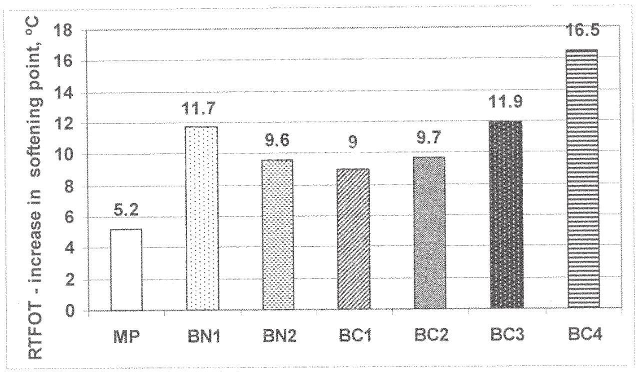

Fig. 8. Influence of oxidation catalyst on softening point increase

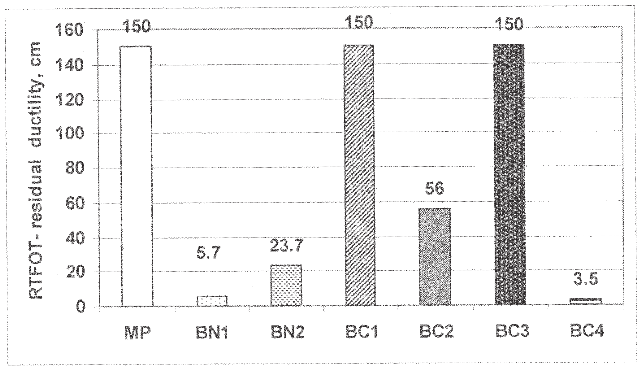

Fig. 9. Influence of oxidation catalyst on residual ductility

in the case of the catalyst based on iron nanoparticles than the one based on iron carboxylate. The presence of aluminum chloride reduces the loss penetration of bitumen oxidation.

Increasing the softening point after applying the aging process is shown in figure 8. It shows a higher variation of the softening point of increasing duration of oxidation, also the increased softening point is higher if catalyst is based on iron nanoparticles han the iron-based carboxylate catalyst. The presence of aluminum chloride favours the growth of the softening point.

Ductility residual variation after applying the aging process is shown in figure 9. It shows a more evident decrease of the bitumen ductility obtained by oxidation of a catalyst of iron nanoparticles, appropriated ductility of bitumen oxidized with iron carboxylate aluminum chloride in the presence of a reaction time of almost more than three times, also ductility reduction is less pronounced in the case of catalyst in the presence of iron nanoparticles with NF8. The presence of aluminum chloride favours the maintaining of high levels of residual ductility lower reaction times.

Conclusions

Getting bitumen by air oxidation was performed in upward air movement in a batch system in a cylindrical reactor, at air WHSV of 40 h^{-1} and a temperature of 180^0 C. Catalytic systems used in the oxidation process were iron nanoparticles, iron carboxylate and aluminum chloride.

Oxidation efficiency was evaluated by determining the main characteristics of road bitumen (penetration, softening point, ductility, Fraass breaking point, asphaltene content and characteristics of aging).

Making this process in the presence of catalysts favours the oxidation reduction in the manufacture of bitumen by blowing air. Catalyst of iron nanoparticles shows a higher efficiency than the type of iron carboxylate (as such or in the presence of aluminum chloride) in the oxidation process.

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