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An environmental friendly anti-ageing additive to bitumen

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HIGHLIGHTS

- Addition of imidazoline to bitumen before ageing reduces oxygen uptake by bitumen.
- Imidazoline decreases asphaltene formation upon aging and its molecular weight.
- Imidazoline improves colloidal stability of bitumen.
- Imidazoline added to bitumen acts as a dispersant and an anti-oxidant.
- Imidazoline can be used as an environmental friendly ageing inhibitor to bitumen.

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ABSTRACT

Oleic imidazoline obtained from natural resource was tested as an ageing inhibitor to bitumen. The effect of oleic imidazoline on the reduction in bitumen oxidative ageing was studied using various analytical methods. Three bitumens of different origin (**O**, **L** and **N**) and their mixes with 1 wt.%. of oleic imidazoline were subjected to ageing by RTFOT method. The aged bitumens with and without imidazoline were analyzed. Colloidal stability of aged bitumens was enhanced by addition of imidazoline confirming the ability of imidazoline to act as a dispersant. GPC analysis of asphaltenes separated from bitumens has confirmed a dispersing ability of imidazoline. The kinetic of oxygen uptake by the bitumens, taken as a determinant of their susceptibility to ageing, showed a decrease in oxygen uptake as a result of imidazoline addition. Amount of oxygen uptake corresponds to ageing index expressed by the viscosity ratios after and before ageing. This indicates that imidazoline can also act as an anti-oxidant to bitumen. Depending on the chemical nature of the bitumen, the dispersant or antioxidant effect of imidazoline prevail. The study has shown that imidazoline can be used as an environmental friendly ageing inhibitor to bitumen.

1. Introduction

Bitumen ageing is a complex phenomenon which involves several processes occurring simultaneously. Resistance to ageing is termed durability. The reactions of bitumen components with atmospheric oxygen make principal contributing factors which are responsible for ageing [1,2]. The rate of oxidative ageing is primarily influenced by temperature. Oxygen reacts with reactive molecules present in bitumen and those reactions produce polar compounds [1,3]. The bitumen oxidation yields principally ketones and sulfoxides. The reactions of bitumen components with oxygen change the generic composition of bitumen. Ageing causes minor changes in the content of saturated components, it decreases the amount of the naphthene-aromatic fraction, while the content of resins may be increased or decreased – depending on the conversion ratio [4–6]. Advancement in bitumen ageing causes reduction in the content of aromatic and polar-aromatic components (resins) and the simultaneous increase in the portion of asphaltenes, and their association. These changes in composition are leading to an increase in the ratio of the continuous to dispersed phase, which finally changes the colloidal structure of bitumen from the sol–gel type to the gel type.

It has been reported that not only the generic composition but also the chemical structure and colloidal stability affect the ageing resistance of bitumen [7].

The changes in the generic composition and chemical structure of bitumen upon ageing cause deterioration of its properties. Binder viscosity and softening point go higher while its penetration and ductility decrease. The most distinct effect on the change in the properties of the binder is exerted by the increased content of polar groups and interactions between those groups leading to

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association. A clear relation has been shown between a higher number of polar functional groups in bitumen during its ageing and bitumen hardness [1]. The carboxylic acids formed on oxidation are adsorbed on mineral aggregates surface and displaced by water [8]. Bitumens that develop greater content of polar groups strongly interacting during ageing fail sooner in the road.

A significant influence also comes from condensation and polymerization of smaller structural units with the formation of a higher molecular weight structures. Association and then agglomeration of asphaltene micelles immobilise particles or micelles, and in consequence bitumen becomes rigid and brittle. The changes in binder properties result in a stiffening of asphalt mix. This leads to a deterioration in performance of the asphalt pavement and consequently to its shorter service time.

Some additives have been found to retard bitumen ageing and may be used as ageing inhibitors [9]. Conventional antioxidants which are free radical scavengers are not effective when used in bitumens because the production and application of asphalt mix are carried out at temperatures below 200 °C, while bitumen oxidation is predominantly a non-free radical reaction under such temperature [10].

Amines, tellurium and selenium oxides, zinc and lead dimethyl- and diethylcarbamates, and hydrated lime, may be used as bitumen ageing inhibitors [9,11]. Also, other compounds or their blends have been suggested as anti-ageing additives for bitumen. Patented was the use of dried grape bagasse which basically comprises phenol, tannins, procyanidins and anthocyanins [12]. According to another invention, addition of lignin to bitumen enhances its anti-ageing capability [13].

Amines were found the most active antioxidants. Derivatives of fatty amines are effective dispersing agents. They react with polar groups in bitumen and prevent interactions between those groups [14]. They can also induce decomposition of the peroxides formed [15].

Ageing inhibitors have so far been employed in bitumen rather seldom in practice. Some compounds perform selectively. A given compound may be an effective inhibitor or it may be completely inactive, depending on the chemical composition of bitumen.

Gawel et al. tested the imidazolines of natural origin (rapeseed oil, oleic acid, lard) as an anti-ageing agent to bitumen [16]. It was shown that addition of imidazoline to bitumen enhances its resistance to ageing as confirmed by the reduction in ageing index. The improvement in bitumen resistance to ageing ranges from a dozen and so to above 40% depending on a kind of imidazoline as well as on chemical nature of bitumen [16]. It was recommended to use oleic imidazoline type I.

The main goal of this work was to study what kind of bitumen - imidazoline interactions are leading to the reduction in oxidative ageing. This knowledge may be useful in application of imidazolines as the environmental friendly anti-ageing additive to bitumen.

2. Materials and procedure

2.1. Materials

Three 50/70 penetration grade bitumens: **O**, **L** and **N** were used in this study. **O** and **L** bitumens were produced from paraffine-naphthenic type Russian crude oil whereas naphthenic type Venezuelan crude was a feedstock for N bitumen production. The main properties of the bitumens are given in Table 1.

Table 1
Bitumen properties.

Properties	Sample		
	O	**L**	**N**
Softening point R&B, °C	49.5	49.5	50.6
Penetration at 25 °C, 0.1 mm	59	61	58
Viscosity at 60 °C, Pas	322	297	433

Oleic imidazoline was applied as an anti-ageing additive. It was selected from six imidazoline samples (rapeseed, oleic and lard imidazolines type I and II) based on the results of improvement in ageing resistance of bitumens due to imidazoline addition [16]. The imidazoline was produced by the Institute of Heavy Organic Synthesis "Blachownia" from oleic acid. The mixture of imidazolines type I and II was used as an anti-ageing additive to bitumen. The proportions of imidazoline type I and II in the product were 59.6:38.4 (w/w), respectively. The rest (2%) consist amides and between-fractions. Content of cationic active substance in imidazoine was 96.8%. The structural formulas of oleic imidazoline type I and II are given in Fig. 1.

2.2. Preparation of bitumen-imidazoline mix

Bitumen sample was heated up to 110 °C, and after addition of imidazoline the components were mixed at this temperature for 30 min. The imidazoline to bitumen proportions in the mix were 1:99 (wt.%). A part of the product obtained was subjected to simulated ageing in laboratory using Rolling Thin-Film Oven Test (RTFOT). To evaluate the effect of imidazoline addition on the bitumen ageing, RTFOT ageing test was also carried out with the bitumen without additive.

3. Methods of analyses

3.1. Colloidal stability

Colloidal stability of the products was determined by Pauli's method [17]. The principle of this method is to precipitate a bitumen sample dissolved in a good solvent (toluene) with an asphaltene precipitant (iso-octane) until precipitation occurs. The onset of asphaltene flocculation/precipitation was measured with a Hitachi U-2001 spectrometer at 740 nm minimum of absorbance. Titration was repeated four times with different bitumen concentrations.

3.2. Acid number

The acid number of bitumen was determined by thermometric titration of the bitumen sample dissolved in toluene and acetone with the potassium hydroxide solution in isopropanol [18]. The method is based on exothermic reaction of acetone conversion into diacetone alcohol, which is catalyzed by hydroxyl ions. Temperature of the titrated solution versus the volume of titrate added was plotted, and volume of titrate corresponding with the equivalence point of titration was taken from the plot.

3.3. Oxygen uptake

Oxygen uptake measurements were performed according to the SHRP method [19]. Glass bottle 60 mL in volume was loaded with 250 mg of bitumen in CH_2Cl_2 and coated on the bottle wall as 40 μm film. Vessel was sealed with rubber cap, wired, and placed in 100 °C bath. After heating for required time, bottle with content was cooled. The sample of gas was withdrawn with a gas-tight syringe and injected into the 504 M chromatograph equipped with 5A zeolite column (length 2 m) and a thermal conductivity detector. To calculate the amount of oxygen consumed, the control analysis was made with gas from bitumen unloaded vessel heated for the same time and cooled. Experiments were carried out with raw bitumen, bitumen with 1 wt.% of imidazoline and imidazoline.

3.4. Separation of asphaltenes

Asphaltene components were precipitated from bitumen samples by 40-fold volume of *n*-heptane according to the IP 143/90 method.

3.5. Analysis of asphaltenes by gel permeation chromatography (GPC)

GPC separation of the asphaltenes was achieved on two Plgel 3 μm MiniMix 4.6 mm × 250 mm columns which was monitored