(54) Title:  METHOD FOR REDUCING BITUMEN ODORS

(57) Abstract:
The invention relates to a method for reducing bitumen odors by admixing active agents and a diluting agent to liquid bitumen, whereby certain aldehydes and alcohols and in addition, if applicable, terpenes, ketones, and carbonic acid esters are used as active agents.
Abstract

The invention relates to a method for reducing bitumen odors by admixing active agents and a diluting agent to liquid bitumen, whereby certain aldehydes and alcohols and in addition, if applicable, terpenes, ketones, and carbonic acid esters are used as active agents.
Method for reducing bitumen odors

The invention relates to a method for reducing bitumen odors by admixing active agents.

Bitumen is a highly-viscous liquid or a solid that consists of hydrocarbons and derivatives thereof. It is soluble in trichloroethylene and softens at temperatures above 100 °C and becomes thin fluid above approximately 150 °C. Bitumen is used on an industrial scale, e.g., as a road topping, whereby a mixture of bitumen and major amounts of stones is applied; moreover, it is used as insulating layer against the penetration of water and moisture into buildings, and for the production of sealing sheeting and tar paper.

In all said applications, bitumen is processed in liquefied form above approximately 140 °C. At these temperatures, most of the volatile substances present in bitumen evaporate, e.g. sulfur and nitrogen compounds that may lead to foul odors.

US-A 5,271,767 describes an odor-free asphalt composition, in which 0.5 to 1 wt.-% of a mixture of
- 10 to 15 wt.-% limonene,
- 85 to 90 wt.-% of a vegetable oil, and
  approximately 2 wt.-% of a silicone oil
are admixed into liquid asphalt (meaning bitumen).
In this context, relatively large amounts of active agents have to be used.

EP-A 1 235 768 describes a composition for odor suppression for hydrocarbons, e.g. asphalt and bitumen, consisting of an aldehyde or ketone and 10 to 90 wt.-% of a carbonic acid alkyl ester. The composition in the example contains a total of 31 wt.-% ester and 60 wt.-% benzaldehyde. Since benzaldehyde is detrimental to
health (see material safety data sheet of Merck of 31 March 2004), this composition is not harmless.

WO 2004/099352 describes additives for odor reduction, e.g. for liquid asphalt cement (meaning bitumen), preferably containing

- 35 to 45 vol.-% limonene,
- 25 to 35 vol.-% pine extract or pine oil,
- 1 to 5 vol.-% Pinus sylvestris oil,
- 3 to 8 vol.-% anise seed oil, and
- 20 to 25 vol.-% of other oils.

Said composition can be diluted with a carrier oil, e.g. a mineral oil, a vegetable oil or a fatty acid alkyl ester. However, it showed that said composition is not optimal for reducing bitumen odors, too.

EP-A 1 772 158 describes a method for reducing foul-smelling substances in tank containers for bitumen, whereby active agents are guided into the gas space over the liquid level together with an inert gas. The active agents can be, e.g., longer-chain aldehydes, ketones, esters or alcohols, e.g. C7 to C12 aldehydes or natural oily essences such as resin oils, and, moreover, perfume-like substances such as vanillin, menthol or alpha-pinene. More detailed specifications concerning the composition of the active agents are not provided therein.

It was therefore the object of the invention to provide a method for reducing bitumen odors, in which relatively small amounts of active agents that are non-objectionable in terms of health are used.

This object is met by the mixture of active agents according to claim 1. It is self-evident that said agents as such should not be foul-smelling, i.e. the selected substances should not bear any, e.g., mercaptan or amino groups.
According to the present invention, the mixture of active agents is not admixed into the gas space, but rather directly into the liquid bitumen which results in higher efficiency.

In the context of the present invention common commercial bitumen is used. Said bitumen might contain residues from crude oil distillation as well as residues that were obtained by means of a cracking process. Naturally occurring bitumen or mixtures of various types of bitumen may be used as well. Examples of bitumen of this type include straight-run asphaltic bitumen, precipitation bitumen, e. g. propane bitumen, oxidized bitumen, naphthene-base bitumen and mixtures thereof. Well-suited bitumen can also be produced by mixing with a naphthene-base or paraffin base flux oil or a vegetable oil. It can just as well contain a polymer such that a polymer-modified bitumen is generated. Well-suited polymers include thermoplastic elastomers or plastomers, such as, e.g. styrene block copolymers and/or olefin copolymers such as ethylene/vinylacetate copolymer.

The aldehyde of component A is selected from

A1. alpha-hexyl cinnamaldehyde (jasmonal H),
A2. 2-(4-tert.-butylbenzyl)propionaldehyde (Lilial), and
A3. 2-benzylidene heptanal (jasminal)

or mixtures thereof. In a particularly preferred embodiment, component A contains all three of the aldehydes specified above.

The other optional aldehydes of component B are preferably selected from:

B1. 3-(4-iso-proplyphenyl)-2-methylpropanal (cyclomaldehyde), particularly in amounts of from 2 to 12 wt.-%, and
B2. 2-methylundecanal, particularly in amounts of from 2 to 8 wt.-%
B3. 2-methyl-3-(3,4-methylene-dioxyphenyl)propanal (helional), particularly in amounts of from 0.5 to 5 wt.-%
or mixtures thereof. In a particularly preferred embodiment, component B contains all three of the aldehydes specified above. Moreover, the aldehydes listed in EP-A 1 235 768 are also well-suited. The amounts of benzaldehyde and citral that are present should preferably be at most 5 wt.-%.

Preferably, naturally occurring alcohols are used as component C. These are preferably selected from

C1. linalol having a boiling point of 198 °C, particularly in amounts of from 5 to 25 wt.-%,
C2. eugenol having a boiling point of 253 °C, particularly in amounts of from 3 to 12 wt.-%,
C3. geraniol having a boiling point of 230 °C, particularly in amounts of from 3 to 12 wt.-%, and
C4. alpha-terpineol having a boiling point of 219 °C, particularly in amounts of from 0.5 to 5 wt.-%

or mixtures thereof. In a particularly preferred embodiment, component C contains all four of the alcohols specified above. Other alcohols, such as vanillin and thymol, are also well-suited.

The optional terpenes of component D are preferably selected from

D1. limonene having a boiling point of 176 °C, particularly in amounts of from 0.5 to 5 wt.-%, and
D2. alpha-pinene having a boiling point of 156 °C, particularly in amounts of from 0,5 to 5 wt.-%

or mixtures thereof. In a particularly preferred embodiment, component D contains both of the terpenes specified above. Terpenes that are present in natural essential oils as well as the terpenes listed in WO-A 2004/099 352 are also well-suited.
Well-suited as ketones in optional component E are e.g.: benzophenone, butylmethyl-ketone, and 1,8-cineol, as well as other ketones that are present in natural essential oils. The ketones listed in WO-A 2004/099 352 are also well-suited.

Well-suited as carbonic acid esters of optional component F are e.g.: benzylsalicylate, amylobutyrate, ethylbutyrate, and amylacetate as well as other carbonic acid esters listed in EP-A 1 235 768.

Preferably a mixture of the active agents and a diluting agent is admixed to the liquid bitumen. Said diluting agent simultaneously acts as mixing mediator during the mixing of the individual components.

The mixture preferably contains 5 to 50, in particular 10 to 40, wt.-% active agents and 95 to 50, in particular 90 to 60, wt.-% diluting agent.

Preferred diluting agents include mineral oils, i.e. hydrocarbon middle distillates, such as, e.g. CATENEX™ made by Shell, as well as vegetable oils such as sunflower oil which consists mainly of linoleic acid. A mixture of CATENEX™ and sunflower oil that is characterized by a particularly high flash point, which reduces the risk of ignition, has also proven to be useful.

Preferably the mixture of active agents and diluting agent is admixed to the liquid bitumen in amounts of from 10 to 200 ppm, in particular from 20 to 180 ppm, and especially in amounts of from 50 to 150 ppm. This is preferably effected at temperatures above 140°C, in particular at temperatures between 150 and 250°C.

Generally, the mixture can be introduced directly into the liquid bitumen that is present in a tank container or a truck. However, since liquid bitumen is usually delivered by truck and filled into the tank container through a hose or preferably a pipe, it is advantageous to introduce the mixture from a reservoir container via a
dosing pump through a side line into the pipe. In this context, the pipe can be split into two channels at one site in the form of a bypass whereby the main amount of the liquid bitumen flows into the channel with the larger diameter, whereas the mixture of active agents and diluting agent is introduced into the narrower bypass channel. This simplifies the dosing and the mixture is better homogenized. This dosing is shown schematically in the drawing. While 1 denotes the bitumen tank, 2 is the truck from which the bitumen is transferred to the tank, 3 is the reservoir container for the mixture containing the active agents, and 4 is the bypass.

It is assumed that the active agents specified above, in particular the aldehydes, undergo a chemical reaction with the foul-smelling substances, e.g. with mercaptans and amines, and thus remove and/or neutralize them.

Using the method according to the invention, the foul smell during the processing of liquid bitumen can be reduced by 60 to 90%, in some cases even by more than 90%, which can be detected by means of olfactory measurement.

**Example 1**

A mixture of active agents is produced from:

- 22.9 parts by weight alpha-hexylcinnamaldehyde
- 19.1 parts by weight 2-benzylidene heptanal
- 9.8 parts by weight 2-(4-tert.-butylbenzyl)propionaldehyde
- 16.5 parts by weight linalol
- 7.7 parts by weight eugenol
- 7.7 parts by weight geraniol
- 7.7 parts by weight 3-(4-iso-propylphenyl)-2-methylpropanal
- 3.1 parts by weight 2-methylundecanal
- 1.9 parts by weight alpha-terpineol
- 1.2 parts by weight limonene
- 1.2 parts by weight 2-methyl-3-(3,4-methylene-dioxyphenyl)-propanal
1.2 parts by weight 2-methyl-3-(3,4-methylene-dioxyphenyl)-propanal
1.2 parts by weight alpha-pinene.

30 parts by weight of this mixture were mixed with 70 parts by weight CATENEX as diluting agent. The flash point (open cup) of this mixture was 165 °C.

A total of 3.75 kg (150 ppm) of the mixture specified above were introduced into a truck containing 25 to liquid bitumen at a temperature of 170°C.

Example 2
30 parts by weight of the mixture from Example 1 were mixed with 70 parts by weight of a mixture of CATENEX and sunflower oil at a ratio of 85 : 15 as diluting agent. The flash point (open cup) of this mixture was 168 °C.

Liquid bitumen was filled from a truck through a pipe into a tank with a capacity of 25 to. Said pipe was divided into two channels with internal diameters of 200 mm and 20 mm, respectively. A total of 2.5 kg (100 ppm) of the mixture specified above were introduced into the narrower channel of the pipe.
1. Method for reducing bitumen odors by admixing active agents and a diluting agent to liquid bitumen, characterized in that the active agents contain:
   A: 20 to 60 wt.-% of an aldehyde which is:
      A1. alpha-hexylcinnamaldehyde,
      A2. 2-(4-tert.-butylibenzyl)propionaldehyde, or
      A3. 2-benzyliden heptanal,
   or mixtures thereof,
   B: 0 to 20 wt.-% of one or more other aldehydes having at least 10 carbon atoms in the molecule,
   C: 10 to 40 wt.-% of one or more alcohols having a boiling point of at least 150°C,
   D: 0 to 20 wt.-% of one or more terpenes having a boiling point of at least 150°C,
   E: 0 to 10 wt.-% of a ketone having a boiling point of at least 150°C, and
   F: 0 to 10 wt.-% of a carbonic acid ester, whereby the percentages add up to 100%.

2. Method according to claim 1, characterized in that the aldehydes of component B are:
   B1. 3-(4-iso-propylphenyl)2-methylpropanal,
   B2. 2-methylundecanal, or
   B3. 2-methyl-3-(3,4-methylene-dioxyphenyl)-propanal
   or mixtures thereof.

3. Method according to claim 1, characterized in that benzaldehyde and citral are present in amounts of at most 5 wt.-%.
4. Method according to claim 1, characterized in that the alcohols of component C are:
   C1. linalol,
   C2. eugenol,
   C3. geraniol, or
   C4. alpha-terpineol
or mixtures thereof.

5. Method according to claim 1, characterized in that the terpenes of component D are:
   D1. limonene or
   D2. alpha-pinene
or mixtures thereof.

6. Method according to claim 1, characterized in that a mixture of
   5 to 50 wt.-% of the active agents and
   95 to 50 wt.-% of a diluting agent
is admixed to liquid bitumen.

7. Method according to claim 6, characterized in that the diluting agent is a mineral oil.

8. Method according to claim 6 or 7, characterized in that 10 to 200 ppm of the mixture of active agents and
diluting agent are admixed to liquid bitumen.

9. Method according to claim 6, 7 or 8, characterized in that the admixing is carried out at temperatures above
   140°C.

10. Bitumen containing 10 to 200 ppm of a mixture of 5 to
    50 wt.-% active agents consisting of
    A: 20 to 60 wt.-% of an aldehyde which is
A1. alpha-hexylcinnamaldehyde,  
A2. 2-(4-tert.-butylbenzyl)propionaldehyde, or  
A3. 2-benzyliden heptanalor mixtures thereof,  
B: 0 to 20 wt.-% of one or more other aldehydes having at least 10 carbon atoms in the molecule,  
C: 10 to 40 wt.-% of one or more naturally-occurring alcohols having a boiling point of at least 150°C,  
D: 0 to 20 wt.-% of one or more terpenes having a boiling point of at least 150°C,  
E: 0 to 10 wt.-% of a ketone having a boiling point of at least 150°C, and  
F: 0 to 10 wt.-% of a carbonic acid ester,  
whereby the percentages add up to 100%, and  
95 to 50 wt.-% of a diluting agent.  

11. Bitumen of claim 10, characterized in that the diluting agent is a mineral oil.