The invention relates to the use of resins, obtained by a reaction of cardanol with a compound of formula (1), where $R_1=H$, COH, COOH, COOR2 or $R_2=R_2=C_1-C_30$ alkyl, $C_2-C_30$ alkenyl, $C_6-C_18$ aryl or $C_7-C_30$ alkaryl with a number average molecular weight of 250 to 100,000 units, in amounts of 0.5 to 10,000 ppm relative to the oil, for the dispersion of asphalts in crude oils or products derived therefrom.
USE OF CARDANOL ALDEHYDE RESINS AS ASPHALT DISPERSANTS IN CRUDE OIL.

[0001] The present invention relates to the use of cardanol-aldehyde resins as asphaltene dispersants in crude oils and asphaltene-containing oils derived from these, and crude oils and residual oils which comprise these resins.

[0002] Asphaltenes are constituents of crude oils. They contain a large number of structures, particularly high molecular weight condensed aromatic components with heteroatoms. In view of the complexity of their chemistry, asphaltenes are described as the oil fraction which is soluble in benzene but not in n-pentane.

[0003] In crude oil, asphaltenes are normally in the form of a colloidal dispersion. This is stabilized by oil resins.

[0004] Asphaltenes can precipitate out during production, refinery, transportation and storage of crude oil and products derived therefrom, such as, for example, heavy fuel oil or marine oil. Common causes for this precipitation are a drop in the temperature or a change in the composition (e.g. evaporation of readily volatile constituents). Asphaltenes can also precipitate out upon flowing through porous media. Flooding with CO₂ during the recovery process can cause asphaltenes to flocculate or to precipitate out.

[0005] Some oils comprise hydrocarbon waxes which precipitate out at low temperatures. Interactions between the precipitation of wax and asphaltenes can increase the overall amount of precipitated substance or its rate of formation.

[0006] Precipitated asphaltenes cause problems during the production and processing of crude oils. Asphaltenes settle out in valves, pipes and conveyors. On hot surfaces, such as, for example, heat exchangers, the carbonization of these precipitates can make their removal very difficult. The precipitates reduce the efficiency of plants and can, in the worst case, lead to complete blockage and to a halt in production, which results in high costs.

[0007] Heavy oils, which are often used for powering ships, comprise considerable amounts of asphaltene. The precipitation of asphaltenes can lead both to poor combustion and also to difficulties with regard to handling and storage of the fuel.

[0008] Bitumens, heavy oils and residues are sometimes diluted with solvents in order to reduce the viscosity for transportation. If asphaltenes precipitate out, then problems arise during handling.

[0009] The precipitation of asphaltenes can be prevented or reduced by small amounts of dispersants. These dispersants display one or more of the following effects:

[0010] a) the amount of precipitate is reduced;
[0011] b) the precipitate is formed more slowly;
[0012] c) the precipitate is more finely divided; and
[0013] d) the tendency of the precipitate to deposit on surfaces is reduced.

[0014] If precipitates of asphaltenes have already formed, they can be removed through the use of solvents. The addition of a dispersant can improve the effectiveness of these solvents.

[0015] A large number of asphaltene dispersants are already known. CA-A-2 029 465 and CA-A-2 075 749 describe alkylphenol formaldehyde resins in combination with hydrophilic-lipophilic vinyl polymers. The asphaltene-dispersing properties of dodecylbenzenesulfonic acid have been described in U.S. Pat. No. 4,414,035, and also by D. L. Chang and H. S. Fogler (SPE paper No. 25185, 1993) and by M. N. Bouts et al. (J. Pet. Technol. 47, 782-7, 1995). Cardanol formaldehyde resins have already been prepared as precursors for crude oil emulsion breakers (U.S. Pat. No. 5,525,201), but were not used as asphaltene dispersants.

[0016] The dispersants known to date can only partially solve the problems caused by the precipitation of asphaltenes. Since oils vary in their composition, individual dispersants can only operate effectively within a limited range. Even small changes in the composition of the oil sometimes have a great effect on the dispersing properties for asphaltenes. For this reason, in some cases the known dispersants are unsatisfactory and additional types are required.

[0017] The object is therefore to provide novel asphaltene dispersants which do not have the described disadvantages of the dispersants known to date.

[0018] Surprisingly, it has been found that cardanol-aldehyde resins can be used in order to prevent the precipitation and/or the deposition of asphaltenes in crude oils and products derived therefrom.

[0019] The invention therefore provides for the use of resins obtainable by reacting cardanol with a compound of the formula (I)

\[
\begin{align*}
\text{R}^\text{O} & \quad \text{H} \\
\text{R} & \quad \text{H}
\end{align*}
\]

(1)

in which

[0021] \(\text{R}^1\) is H, CHO, COOH, COOR² or R², and

[0022] \(\text{R}^2\) is C₁-C₃₀-alkyl, C₇-C₃₀-alkenyl, C₆-C₃₀-aryl or C₇-C₃₀-alkylaryl, and which have a number-average molecular weight of from 250 to 100 000 units, in amounts of from 0.5 to 10 000 ppm, based on the oil, for dispersing asphaltenes in crude oils or products derived therefrom.

[0023] The invention further provides crude oils and products derived from these which comprise 0.5 to 10 000 ppm of the resins defined above.

[0024] The invention further provides a process for dispersing asphaltenes in crude oils and products derived therefrom by adding 0.5 to 10 000 ppm of the resins defined above to the oils.
The compounds according to the invention are, for example, those of the formulae 2 to 5.

If glyoxal is used for the condensation, then the radical $R^3$ is initially OH. The resulting free OH group can additionally also be esterified or etherified, so that $R^2$ can have the meaning O-alkyl, O-aryl, O-alkenyl, O-alkylary, OCO-alkyl, OCO-aryl, OCO-alkenyl, OCO-alkaryl. Corresponding compounds prepared by subsequent etherification of the resins are likewise covered by the subject-matter of the present invention. The terms "alkyl", "alkenyl", "aryl" and "alkylary" are to be understood as given for the definition of $R^2$. $R^3$ can also have the same meaning as is given for $R^2$ and $R^3$.

Cardanol is a constituent of oil that is obtained from the shell of cashew kernels. Its main constituent is an alkyphenol of the formula 6.

$X$ is a hydrocarbon chain with about 15 carbon atoms and 1 to 3 double bonds, as disclosed, for example, in R. Ikeda et al., Macromol. Rapid Commun. 21, 496-499 (2000) and A. Mahannar, Journal of Applied Polymer Science, 61, 2107-2111 (1996).

$R^2$ is preferably an alkynyl or alkyl radical, a chain length of from 6 to 24, particularly preferably 8 to 22, specifically 12 to 18 carbon atoms. Alkynyl and alkynyl radicals can either be linear or branched.

If $R^2$ is an alkylaryl radical, then alkylaryl is preferably a radical, bonded by the aromatic ring, whose aromatic ring preferably comprises 6 carbon atoms, and which carries, in the ortho, meta or para position relative to the bond mentioned above, an alkyl radical with a chain length of preferably 1 to 18, particularly preferably 4 to 16, in particular 6 to 12, carbon atoms.

Products derived from crude oils are, for example, heavy fuel oil, marine oil or bitumen.

As well as resins based on pure cardanol, condensates of mixtures of cardanol and alkyphenols of the formula (7) with compounds according to formula 1 also act as asphaltene dispersants.

In which $R^4$ and OH may be in the ortho, meta or para position relative to one another, and $R^1$ is C$_1$- to C$_{16}$-alkyl, C$_{10}$- to C$_{16}$-alkenyl, C$_8$- to C$_{18}$-aryl or C$_7$- to C$_{13}$-alkylaryl. Particular effectiveness is displayed by resins based on the cardanol/alkyphenol mixtures with para cresol, para-ethylphenol, para-isopropylphenol, para-tert-butylphenol, para-isocetylphenol, para-isononylphenol, para-isododecylphenol, para-phenylphenol and para-cumylphenol in the ratios 1:100 to 100:1, preferably 1:10 to 10:1, particularly preferably 1:5 to 5:1, specifically 2:1 to 1:2, in particular 1:1.

The resins according to the invention are generally prepared by acid- or alkaline-catalyzed condensation of cardanol with the corresponding aldehydes. The reaction temperature is generally between 50 and 170°C, preferably 120 to 165°C. The reaction is normally carried out at atmospheric pressure. The catalyzing acids are, for example, HCl, H$_2$SO$_4$, sulfonic acids or H$_3$PO$_4$, and the bases are NaOH, KOH or triethylamine, which are used in amounts of from 0.1 to 50% by weight, based on the weight of the reaction mixture. The condensation generally requires 30 min to 6 hours. The molar ratio between aldehyde and cardanol is generally from 0.5:1 to 4:1, preferably from 0.8:1 to 1.8:1.

The dispersant according to the invention is used in a concentration of from 0.5 to 10 000 ppm, preferably from 2 to 2000 ppm.

For easier dosing, the dispersant can be formulated as a solution in an oil-miscible solvent, such as, for example,
aromatic hydrocarbons or mixtures of hydrocarbons and an aliphatic alcohol. In addition to the dispersant according to the invention, it is also possible to use alkylyphenol-formaldehyde resins, oxalkylated amines, wax dispersants or any mixtures thereof. It is likewise possible to use other organic acids with surfactant properties, such as, for example, mono- or dialkylbenzenesulfonic acids, petroleum sulfonic acids and alkanesulfonic acids as additional components.

EXAMPLES

Example 1

Reaction of Cardanol with Formaldehyde

100.0 g of cardanol (M=302), 100 ml of an aromatic solvent and 1.1 g of alkylbenzenesulfonic acid (0.5 mol %) were initially introduced into a 500 ml four-necked flask fitted with contact thermometer, stirrer, dropping funnel and water separator. With stirring and nitrogenblanketing, the reaction mixture was heated to 120° C. and, at this temperature, 26.8 g of aqueous formaldehyde solution (37% strength) were slowly added dropwise. When the addition was complete, the mixture was stirred for one hour at 120° C. and for one hour at 165° C. and the water of reaction which formed was removed by means of the separator. The product was evaporated to dryness on a rotary evaporator (yield: 107.2 g) and analyzed by means of GPC.

Example 2

Reaction of Cardanol with Glyoxal

100.0 g of cardanol (M=302), 100 ml of an aromatic solvent and 1.1 g of alkylbenzenesulfonic acid (0.5 mol %) were initially introduced into a 500 ml four-necked flask fitted with contact thermometer, stirrer, dropping funnel and water separator. With stirring and nitrogenblanketing, the reaction mixture was heated to 120° C. and, at this temperature, 19.3 g of aqueous glyoxal solution (50% strength) were slowly added dropwise. When the addition was complete, the mixture was stirred for one hour at 120° C. and for one hour at 165° C. and the water of reaction which formed was removed by means of the separator. The product was evaporated to dryness on a rotary evaporator (yield: 102.8 g) and analyzed by means of GPC.

Example 3

Reaction of Cardanol with Glyoxylic Acid

100.0 g of cardanol (M=302), 100 ml of an aromatic solvent and 1.1 g of alkylbenzenesulfonic acid (0.5 mol %) were initially introduced into a 500 ml four-necked flask fitted with contact thermometer, stirrer, dropping funnel and water separator. With stirring and nitrogenblanketing, the reaction mixture was heated to 120° C. and, at this temperature, 17.3 g of aqueous glyoxylic acid solution (50% strength) were slowly added dropwise. When the addition was complete, the mixture was stirred for one hour at 120° C. and for one hour at 165° C. and the water of reaction which formed was removed by means of the separator. The product was evaporated to dryness on a rotary evaporator (yield: 107.3 g) and analyzed by means of GPC.

Example 4

Reaction of Cardanol and Para-isononylphenol with Formaldehyde

50.0 g of cardanol (M=302), 50.0 g of para-isononylphenol (M=220), 100 ml of an aromatic solvent and 1.1 g of alkylbenzenesulfonic acid (0.5 mol %) were initially introduced into a 500 ml four-necked flask fitted with contact thermometer, stirrer, dropping funnel and water separator. With stirring and nitrogen blanketing, the reaction mixture was heated to 120° C. and, at this temperature, 23.2 g of aqueous formaldehyde solution (37% strength) were slowly added dropwise. When the addition was complete, the mixture was stirred for one hour at 120° C. and for one hour at 165° C. and the water of reaction which formed was removed by means of the separator. The product was evaporated to dryness on a rotary evaporator (yield: 104.9 g) and analyzed by means of GPC.

Example 5

Reaction of Cardanol and Para-Cumylphenol with Formaldehyde

50.0 g of cardanol (M=302), 50.0 g of para-cumylphenol (M=212), 100 ml of an aromatic solvent and 1.1 g of alkylbenzenesulfonic acid (0.5 mol %) were initially introduced into a 500 ml four-necked flask fitted with contact thermometer, stirrer, dropping funnel and water separator. With stirring and nitrogen blanketing, the reaction mixture was heated to 120° C. and, at this temperature, 22.8 g of aqueous formaldehyde solution (37% strength) were slowly added dropwise. When the addition was complete, the mixture was stirred for one hour at 120° C. and for one hour at 165° C. and the water of reaction which formed was removed by means of the separator. The product was evaporated to dryness on a rotary evaporator (yield: 104.9 g) and analyzed by means of GPC.

Example 6

Reaction of Cardanol with Dodecyl Glyoxalate

100.0 g of cardanol (M=302) and 0.5 g of alkylbenzenesulfonic acid (0.5 mol %) were dissolved in 100 g of an aromatic solvent in a 1000 ml stirrable flask fitted with contact thermometer, stirrer, dropping funnel and water separator. With stirring and nitrogen blanketing, the reaction mixture was heated to 120° C. At 120° C, 75.6 g of dodecyl glyoxalate (M=242) in 100 g of an aromatic solvent were slowly added dropwise. When the addition was complete, the mixture was after-reacted for one hour at 120° C. and for one hour at 165° C. The water of reaction which formed was removed by means of the water separator. The product was evaporated to dryness on a rotary evaporator (yield: 168.4 g) and analyzed by means of GPC.

Testing the Effectiveness of Asphaltene Dispersants

Principle of the Dispersion Test

Dispersion and precipitation of asphaltenes depends on the nature of the hydrocarbon medium. Asphaltenes are soluble in aromatic hydrocarbons, but not in aliphatic hydrocarbons. It is thus possible to test dispersants by dissolving the oil or extracted asphaltenes in an aromatic solvent and then adding an aliphatic hydrocarbon in order to produce a precipitate. Since asphaltenes are darker in color, the amount of precipitate can be determined by means of a colorimetric measurement of the supernatant liquid. The darker the supernatant liquid, the more asphaltenes remain dispersed, i.e. the better the dispersant. This test is described
in CA-A-2 029 465. In our version of the test, the precipitation medium is chosen so that the asphaltenes precipitate out for the most part, but not completely. The dispersion test is carried out according to steps a) to f):

- **[0046]** a) A 25% strength oil solution in toluene is filtered in order to remove impurities.

- **[0047]** b) Initially introduce 9.5 ml of heptane as precipitating agent for asphaltenes and 0.5 ml of toluene/dispersant mixture (25:1) into a small graduated glass tube which easily holds 10 ml and shake well. This corresponds to a dispersant concentration of 2000 ppm. The amount of dispersant can be varied as required. Pure toluene is used for the blanks.

- **[0048]** c) 0.1 ml of the filtered oil solution is then added to the small glass tube and likewise shaken well.

- **[0049]** d) Leave the sample to stand for 2 hours without disruption in order that the precipitated asphaltenes can collect at the bottom of the tube.

- **[0050]** e) After this time has lapsed, the volume of the sediment is estimated using the graduations, the appearance of the overall sample is recorded and then 1 ml is carefully taken up using a pipette from the supernatant phase.

- **[0051]** f) The amount pipetted off is dissolved in 5 ml of a 99:1 toluene/triethanolamine mixture and measured photometrically at 600 nm.

**[0052]** Evaluation of the Dispersion Test

**[0053]** The dispersion A) is calculated using the following equation:

\[
A = 100 \times \frac{(D-D_0)}{D_0}
\]

**[0054]** Where D and D₀ are the optical density of the measurement solution and blank. The maximum achievable value of A, Aₘₐₓ, corresponds to complete dispersion of the asphaltenes. It can be estimated by carrying out an experiment without dispersant, with toluene instead of heptane— as a result the asphaltenes remain completely dispersed. The volume of the sediment gives further information regarding the effectiveness of the dispersant. The smaller the amount of sediment, the better dispersed is the substance.

**[0055]** Dispersion Effect of the Example compounds

**[0056]** Using an asphaltene-rich oil from Venezuela, substances according to the invention were tested using the dispersion test. The dispersion concentration was 2000 ppm. In this experimental series, the maximum dispersion effect Aₘₐₓ was about 99.5%.

1. The use of resins obtainable by reacting cardanol with a compound of the formula (1)

\[
\text{OH}
\]

\[
\begin{align*}
\text{R}^1 \quad \text{H} \\
\text{R}^1 \quad \text{CHO} \\
\text{R}^1 \quad \text{COOH} \\
\text{R}^1 \quad \text{COOR} \\
\text{R}^1 \quad \text{R}^2
\end{align*}
\]

R¹ is H, CHO, COOH, COOR² or R², and

R² is C₅-C₇-alkyl, C₇-C₉-alkenyl, C₇-C₉-aryl or C₇-C₉-alkylaryl, and which have a number-average molecular weight of from 250 to 100 000 units, in amounts of from 0.5 to 10 000 ppm, based on the oil, for dispersing asphaltenes in crude oils or products derived therefrom.

2. The use as claimed in claim 1, where cardanol is reacted in a mixture with alkylphenols of the formula (7) in the ratio 100:1 to 1:100

\[
\begin{align*}
\text{R}^1 \quad \text{OH} \\
\text{R}^2
\end{align*}
\]

in which R¹ and OH may be in the ortho, meta or para position relative to one another, and R² is C₅-C₇-alkyl, C₇-C₉-alkenyl, C₇-C₉-aryl or C₇-C₉-alkylaryl.

3. The use as claimed in claim 1 and/or 2, where R¹ is an alkyl or aromatic radical having 6 to 24 carbon atoms.

4. The use as claimed in one or more of claims 1 and/or 2, where R¹ is CHO.

5. The use as claimed in claim 4, where the resin obtained from the reaction is esterified or etherified.

6. A process for dispersing asphaltenes in crude oils and products derived therefrom, which comprises adding cardanol-aldehyde resins as claimed in one or more of claims 1 to 5 in an amount of from 0.5 to 10 000 ppm.

7. The process as claimed in claim 6, wherein alkylphenoformaldehyde resins, oxaalkylated amines, mono- or dialkylsulfonic acids, petroleum acids, alkane sulfonic acids, wax dispersant or any mixtures thereof are additionally used.

8. A crude oil or a product derived therefrom comprising an asphaltene dispersant as claimed in one or more of claims 1 to 5.