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(54) Process for decolouring a cracked distillate

(57) The invention relates to the decolouring of cracked distillate, by contacting the distillate with nitric acid, washing the cracked distillate fraction, during which the nitric acid is removed, and subsequently evaporating and condensing the cracked distillate fraction. The invention also relates to a resin obtainable from a cracked distillate decoloured according to the process of the invention.

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Description

The invention relates to a process for decolouring a cracked distillate which comprises the following steps:

a) contacting the cracked distillate with an acid, whereby a cracked distillate fraction is formed, and
b) evaporating and condensing the cracked distillate fraction thus formed.

In particular, the invention relates to a process for decolouring a cracked distillate that is suitable for the production of hydrocarbon resins, especially for the production of hydrocarbon resins that are used as adhesives in glues. Cracked distillate generally contains contaminations, as a result of which it has a more or less yellow to brown colour. A method for decolouring cracked distillate is described in EP-A-233,074.

In EP-A-233,074 a cracked distillate with a boiling range between 80 and 260°C is decoloured by contacting it with 0.1-1% sulphuric acid. Then the cracked distillate thus obtained is vacuum-distilled, whereby an aromatic fraction with a boiling range of between 80 and 260°C is separated off. This sulphuric-acid treatment, optionally followed by vacuum-distillation, is repeated at least once. Depending on the number of times that the cracked distillate is treated with sulphuric acid and on whether the cracked distillate is distilled after each sulphuric acid treatment, the condensate yield is between 37 and 87%. The best decolouring described in EP-A-233,074 was obtained after four acid treatments and one distillation. The yield after this treatment was 50% and the colour of a resin produced from this charge was 3.7 on Gardner's scale.

A drawback of the process described in EP-A-233,074 is that the yield of decoloured cracked distillate is relatively low.

The aim of the invention is to provide a process for decolouring a cracked distillate that does not present said drawback.

This aim is achieved according to the invention in that the acid is nitric acid and is used in an amount of at least 1 part by weight of nitric acid per 100 parts by weight of the cracked distillate and the cracked distillate fraction is washed between steps (a) and (b), during which the nitric acid and the reaction products of the nitric acid are removed from it.

This results in an entirely or almost entirely decoloured cracked distillate in a yield of at least 90 wt.%.

An advantage of the process according to the invention is that after the evaporation a residue remains that has a considerably smaller volume than the residue remaining with the known methods for decolouring cracked distillates. In view of the high costs of destroying waste products, this implies a considerable economic advantage.

A further advantage of the invention is that the degree of unsaturation of the cracked distillate obtained according to the process of the invention is higher than that of the untreated cracked distillate, which means that the decoloured cracked distillate is more suitable for the production of hydrocarbon resins.

Where the term 'cracked distillate' is used in the above and below, this is understood to be the by-product obtained in the thermal cracking of a cracker feedstock, which by-product comprises a mixture of hydrocarbons with a boiling range of between 80 and 260°C, at least 35 wt.% of which consists of unsaturated hydrocarbons. 'Cracked distillate' is also understood to be a fraction of unsaturated compounds that can be polymerised into a resin, obtained from distillation of coal tar. A 'cracker feedstock' is understood to be a mixture of hydrocarbons. Examples of cracker feedstocks are ethylene, 3C fractions, 4C fractions, naphtha and gas condensates. The unsaturated compounds in a cracked distillate suitable for the production of a resin that can be used as an adhesive in glues may be: methyl vinyl benzene, indene, naphthalene, isopropenylbenzene, styrene and dicyclopentadiene. In general, several unsaturated compounds are present, not one of these compounds constituting more than 50 wt.% of the cracked distillate. A cracked distillate that is suitable for the production of a resin preferably contains at least 10 wt.% methyl vinyl benzene and 10% indene and at most 10 wt.% styrene, 10% isopropenylbenzene, 5% dicyclopentadiene and 20 wt.% naphthalene.

The decolouring of styrene has been known from NL-A-7,109,804 since 1972. In that patent styrene is decoloured by contacting it with nitric acid. The 99 wt.% pure styrene was obtained by distilling, with extraction, a fraction obtained in fractional distillation of a cracked distillate, using a polar organic solvent with which styrene and xylene can be separated. NL-A-7,109,804 nowhere describes or suggests that the described process for decolouring styrene can also be used for decolouring other fractions, let alone that this process might be suitable for decolouring a cracked distillate that contains less than 50 wt.% styrene, that has a wide boiling range or that is suitable for the production of hydrocarbon resins. Excluded from the process according to the invention is a cracked distillate containing more than 50 wt.% styrene. Preferably the cracked distillate contains less than 20 wt.% and more preferably not more than 10 wt.% styrene.

Patent applications in the field of decolouring hydrocarbon resins and hydrocarbons suitable for such resins have appeared regularly (on average more than 1 per year) since 1972. In spite of the evident need for a suitable process for the preparation of a decoloured resin, no one has so far had the insight to use the method described in NL-A-7,109,804 to decolour cracked distillate for the preparation of hydrocarbon resins. Since the publication of NL-A-7,109,804, the technical developments have rather moved in an entirely different direction, namely in the direction of decolouring the

hydrocarbon resins themselves. In particular, many patent applications in the field of decolouring the resin by means of hydrogenation have been published. The hydrogenation of hydrocarbon resins is described for example in US-A-4,276,396, JP-A-61,028,508, JP-A-04,335,014 and in WO-A-9,512,623. As the resin has a high viscosity, the hydrogenation, which usually takes several hours, is often carried out in solution, at elevated temperature and pressure. The hydrogenation of the low-molecular, much less viscous cracked distillate itself does not offer a solution, because a saturated cracked distillate can no longer be polymerised into a resin. Advantages of hydrogenating the resin over treating the cracked distillate with sulphuric acid are that the yield is much higher and there is no risk of the reaction running out of control owing to excessive heat development.

Advantages of the process according to the invention over hydrogenating the resin are that the process according to the invention can be carried out at room temperature and atmospheric pressure and takes much less time.

A further advantage of the process according to the invention is that only cheap reagents are required as nitric acid and means for washing the fraction containing the cracked distillate, for example with water. This in contrast to the relatively expensive hydrogen that is required to hydrogenate the resin.

In the process according to the invention the cracked distillate is contacted with at least 1 wt.% nitric acid. 'Nitric acid' is here and hereafter understood to be an at least 50 wt.% solution of HNO_3 in water. Cracked distillate and nitric acid can be brought into contact with one another by vigorously stirring a mixture of the two substances. When the cracked distillate is contacted with less than 1 wt.% nitric acid, the effect of the decolouring decreases. The amount of nitric acid with which the cracked distillate must be contacted depends on the degree of decolouring and can easily be experimentally determined by one skilled in the art.

Preferably the cracked distillate is contacted with at most 5 wt.% nitric acid. It has been found that contacting the cracked distillate with more than 5 wt.% nitric acid is detrimental to the yield of decoloured cracked distillate.

The length of time for which the cracked distillate is contacted with the nitric acid and the temperature at which this takes place are not very critical for the decolouring of the cracked distillate and can be chosen in wide ranges by one skilled in the art. Preferably the cracked distillate is contacted with nitric acid for 1-20 minutes, at a temperature of between 0 and 50°C. With shorter times or/and lower temperatures incomplete decolouring takes place, whereas with longer times or/and higher temperatures the cracked distillate polymerises, which results in a lower yield.

After the cracked distillate and the nitric acid have been contacted with one another and after the optional stirring has been stopped, spontaneous demixing takes place into a cracked distillate fraction and a nitric acid fraction. The heavier nitric acid fraction can be entirely or partly drained.

In the process according to the invention the cracked distillate fraction is subsequently washed. The washing of the cracked distillate fraction, in which residual nitric acid and the reaction products of nitric acid are removed, is necessary to prevent polymerisation of the cracked distillate during the subsequent evaporation, to be discussed below. Said washing can be carried out with water. The effect of the washing can be enhanced by vigorously stirring a mixture of cracked distillate and water. After the stirring, the mixture will spontaneously separate into a cracked distillate fraction and a fraction containing residual nitric acid and reaction products of the nitric acid. The latter, heavier fraction can easily be drained.

The cracked distillate fraction is preferably washed with an alkaline solution. The strength and amount can be chosen so as to cause the nitric acid still present to be converted into a salt in its entirety. To this end the addition of the alkaline solution can for example continue for so long until the mixture's pH becomes higher than 7. This ensures that the cracked distillate yield after the evaporation and condensation is greater than when the evaporation takes place from an acid environment. A further advantage of washing with an alkaline solution is that, during the evaporation and condensation of the cracked distillate fraction, the installation in which this takes place is not affected by nitric acid vapours.

If an excess of the alkaline solution is added it is preferable to wash the cracked distillate fraction with water after separation of the excess alkaline solution. This protects an evaporator, in which the cracked distillate fraction is subsequently evaporated, against attack by residual caustic still present.

Preferably the nitric acid still present is just neutralised. This facilitates the demixing of the cracked distillate fraction and the water phase. The nitric acid still present can be just neutralised by slowly adding the alkaline solution with vigorous stirring, while the mixture's pH is measured and the addition is stopped when the pH becomes 7.

In the process according to the invention the cracked distillate fraction thus obtained is subsequently evaporated and condensed. Depending on the composition of the cracked distillate, the pressure can be reduced in this step, so that the cracked distillate fraction evaporates at a lower temperature. A too high temperature in the evaporation of the cracked distillate presents the drawback that oligomerisation takes place. Preferably the temperature during evaporation is not higher than 100°C.

The evaporation and condensation of the cracked distillate fraction can be continued for as long as an entirely or almost entirely decoloured condensate is obtained. The compounds that were responsible for the cracked distillate's colour then remain behind in a resi-

due. At what residue the evaporation can be stopped can be easily determined on the basis of the residue's viscosity. If the residue's viscosity becomes too high, this results in inhomogeneous heating of the residue. The effect of this is that parts of the residue have a higher temperature than desired, as a result of which oligomerisation may take place. It has been found that, after evaporation at approx. 80°C, the residue's viscosity did not yet increase appreciably at a residue of 10 wt.% of the original amount of cracked distillate.

The residue, which, in addition to nitric acid compounds, also contains oligomers, can for example be burned. An environmental advantage is that, besides water and carbon dioxide, only nitrogen oxides are released in the burning of the residue. It is much easier to separate nitrogen oxides from water and carbon dioxide than the sulphur dioxide that is released in the burning of the residue formed in the process described in EP-A-233,074.

The invention also relates to a hydrocarbon resin obtainable from a cracked distillate that has been decoloured by the process according to the invention. This resin can be obtained by cationically polymerising the decoloured cracked distillate into a resin. Such a polymerisation is known and is described in for example EP-A-233,074. This describes a hydrocarbon resin produced from cracked distillates treated with sulphuric acid. The most colourless resin prepared according to this process described herein has a colour with a Gardner value of 3.8.

An advantage of the resin according to the invention is that it has a colour with a Gardner value of less than 1.

The invention is elucidated with reference to an example.

The Gardner value in which the colours of the cracked distillate and the resin are expressed was measured according to ASTM D-1544.

All the percentages mentioned in the example are percentages by weight.

Example I

A cracked distillate with a Gardner value of 8 and a degree of unsaturation of approx. 65%, which contains, among other compounds: 28% methyl vinyl benzene, 30% indene, 1% styrene, 4% isopropenylbenzene, 1% naphthalene and less than 0.5% dicyclopentadiene, is contacted with 2% (based on the cracked distillate) nitric acid (a 63% solution of HNO_3 in water) for 5 minutes at 30°C. After 15 minutes' demixing, 45% of the nitric acid was drained. 4.6% sodium hydroxide (a 10% solution of NaOH in water) was added to the cracked distillate fraction. The mixture was shown to have a pH of over 7 with the aid of litmus paper. After 20 minutes' demixing, 97% of the caustic phase was drained. Then the cracked distillate fraction was washed with 5% (based on the cracked distillate) water. After 15 minutes the water was drained.

The washed cracked distillate was evaporated at a bottom temperature of between 60 and 70°C and a pressure of 10 mbar, with 1 tray being present as a demister. The evaporation was stopped at the moment that 10% residue still remained in the evaporator.

The condensate, which had a 66% degree of unsaturation, contained the following compounds: 30% methyl vinyl benzene, 30% indene, 1% styrene, 4% isopropenylbenzene, 0.3% naphthalene and less than 0.5% dicyclopentadiene. The unsaturation of the condensed cracked distillate proves to have increased, while the Gardner value is less than 1.

Claims

1. Process for decolouring a cracked distillate that comprises the following steps:

   a) contacting the cracked distillate with an acid, whereby a cracked distillate fraction is formed, and
   b) evaporating and condensing the cracked distillate fraction, characterised in that the acid is nitric acid and is used in an amount of at least 1 part by weight of nitric acid per 100 parts by weight of the cracked distillate and the cracked distillate fraction is washed between steps (a) and (b), during which the nitric acid and the reaction products of the nitric acid are removed from it, the cracked distillate containing at most 50 wt.% styrene.

2. Process according to Claim 1, in which the cracked distillate contains at most 10 wt.% styrene and 5% dicyclopentadiene.

3. Process according to Claim 1 or Claim 2, in which the cracked distillate is contacted with at most 5 wt.% nitric acid.

4. Process according to any one of Claims 1-3, in which the cracked distillate is in contact with the nitric acid for 1-20 minutes, at 0-50°C.

5. Process according to any one of Claims 1-4, in which the cracked distillate fraction is washed with an alkaline solution.

6. Hydrocarbon resin obtainable from cracked distillate, decoloured according to the process of any one of Claims 1-5.

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EUROPEAN SEARCH REPORT

Application Number
EP 97 20 0007

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
D,Y	US 3 763 015 A (TORAY INDUSTRIES) * the whole document * ---	1-6	C10G17/04 C10G70/00 C08F240/00
D,Y	EP 0 233 074 A (EXXON) * claim 17 * -----	1-6	

TECHNICAL FIELDS SEARCHED (Int.Cl.6)

C10G
C08F

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	21 March 1997	Michiels, P

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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A : technological background
O : non-written disclosure
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T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
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L : document cited for other reasons

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