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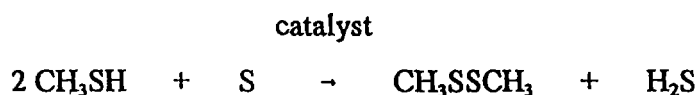
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"COMPOSITIONS BASED ON DIMETHYL DISULPHIDE WITH A MASKED SMELL"

The present invention relates to organic sulphides and more particularly to dimethyl disulphide.

Dimethyl disulphide (DMDS) has a strong and aggressive smell due in part to the presence of highly odorous impurities and in part to the garlicky and ethereal smell intrinsic to DMDS. This strong smell hinders the increased use of this product in applications such as the sulphurization of catalysts or as a loading additive for steam cracking. In comparison with other products used in these applications, such as tert-alkyl polysulphides, DMDS exhibits numerous advantages, in particular a high sulphur content (68%) and non-coking degradation products (CH_4 and H_2S). Furthermore, in these applications, the performance of DMDS is generally superior to that of other products, such as tert-alkyl polysulphides. However, these other products have markedly lower odorous levels and are, therefore, easier to handle than DMDS.

A particularly efficient and economical method, among the methods for the synthesis of DMDS, is the oxidation of methyl mercaptan by sulphur according to the reaction:



This oxidation of methyl mercaptan by sulphur, catalysed by organic or inorganic, homogeneous or heterogeneous, basic agents under batchwise or continuous conditions, is accompanied by a release of hydrogen sulphide and of dimethyl polysulphides ($\text{CH}_3\text{S}_x\text{CH}_3$) with a sulphur rank x of greater than 2. In order to manufacture DMDS according to this process with high yields and a limited production of DMPS (dimethyl polysulphides with a rank greater than 2), European patent specification 0,446,109, the contents of which are incorporated here by reference, discloses a preparation process comprising two reaction regions interrupted by an intermediate degassing region and followed by a distillation region. Although giving a good performance in terms of yield and selectivity for DMDS, the process results in a not insignificant amount of methyl mercaptan (approximately



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4000 ppm) and a very small amount of dimethyl sulphide (approximately 300 ppm), originating from the methyl mercaptan used or produced during the synthesis of DMDS, being left in the finished product. These volatile impurities render the smell of the DMDS very unpleasant and aggressive and this strong smell is regarded as a significant cause of difficulties during the handling of this product.

In order to mask the smell of organic polysulphides, US patent specification 5,559,271 recommends adding a certain amount of masking product to them, such as, in particular, vanillin or ethyl vanillin. Although its general formula includes DMDS, this patent specification is more particularly targeted at the treatment of heavy polysulphides, such as, for example, di-t-nonyl pentasulphide. The application of the method of this patent specification to DMDS does not allow its nauseating and highly unpleasant smell to be masked.

It has now been found that, in the specific case of DMDS, the addition of an odour-masking agent is only effective if the DMDS used has a reduced content of highly odorous volatile impurities, such as methyl mercaptan and dimethyl sulphide, and preferably comprises less than 200 ppm by weight of methyl mercaptan and less than 50 ppm by weight of dimethyl sulphide. It has also been found that the most effective odour-masking agents are not those mentioned in the abovementioned US patent specification but those chosen from the esters corresponding to the general formula:



in which R^1 represents an unsaturated or saturated, linear or branched hydrocarbon-comprising radical containing from 1 to 4 carbon atoms and R^2 represents an unsaturated or saturated, linear, branched or cyclic hydrocarbon-comprising radical containing from 2 to 8 carbon atoms.

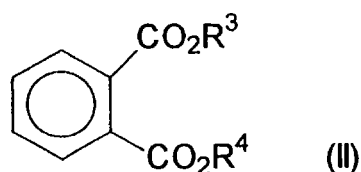
According to the present invention there is provided a dimethyl disulphide (DMDS) composition comprising, by weight, at least 95% of dimethyl disulphide, less than 500 ppm of methyl mercaptan (MM), less than 100 ppm of dimethyl sulphide (DMS) and not more than 1% of at least one odour-masking agent. Preferably the odour-masking agent is an ester of general formula (I) as defined above.

Any method known to a person skilled in the art for producing a DMDS with a reduced content of volatile impurities, such as MM and DMS, can be used to prepare DMDS for use in the compositions of the present invention. However, when DMDS for use in the compositions of the present invention is prepared from a DMDS comprising high contents of MM and DMS, a particularly preferred method comprises a distillative topping. This method has the advantage of removing both MM and DMS, whereas the usual methods for smell reduction, generally based on removing residual mercaptans by specific reaction of a mercaptan functional group with a removal agent, such as a base or an alkene oxide in the presence of a base, are without effect on DMS present in DMDS.

The DMDS, thus topped, which preferably comprises less than 200 ppm of MM and less than 50 ppm of DMS, is used to prepare a composition according to the invention by simple addition of at least one odour-masking agent.

One of the main advantages of DMDS in its applications is its high sulphur content (68%). Use of an excessively high amount of odour-masking agent would result in this sulphur assay being lowered, thus reducing the advantage of this product. The maximum content of odour-masking agent(s) is therefore set at 1% but this content is preferably between 0.1 and 0.5% and more particularly approximately 0.2%.

Suitable esters of general formula (I) for use according to the present invention include, butyl acetate, isoamyl acetate, benzyl acetate, ethyl butyrate, propyl butyrate, butyl butyrate, 2-methylbutyl butyrate or isoamyl butyrate. Isoamyl acetate, 2-methylbutyl butyrate, isoamyl butyrate, benzyl acetate and mixtures thereof are more particularly preferred. The esters (I) may optionally be used in combination with an ortho-phthalate of general formula:



in which each of R^3 and R^4 , which may be the same or different, represents an unsaturated or saturated, linear, branched or cyclic hydrocarbon-comprising radical containing from 1 to 8 carbon atoms. Mention may more particularly be made, as a non-limiting example of compound (II), of diethyl ortho-phthalate.

A typical composition of the present invention comprises, by weight:

isoamyl acetate	:	0.1%
diethyl ortho-phthalate:		0.1%
topped DMDS	:	99.8%

Another typical composition of the present invention comprises, by weight:

isoamyl acetate	:	0.05%
2-methylbutyl butyrate	:	0.03%
benzyl acetate :		0.02%
diethyl ortho-phthalate:		0.1%
topped DMDS	:	99.8%

The dimethyl disulphide compositions according to the present invention may be prepared by a process which comprises preparing dimethyl disulphide with a reduced content of volatile impurities and adding at least one odour-masking agent, such that a dimethyl disulphide composition comprising, by weight, at least 95% of dimethyl disulphide, less than 500 ppm of methyl mercaptan, less than 100 ppm of dimethyl sulphide and not more than 1% of at least one odour-masking agent is obtained.

The invention is further illustrated by way of example with reference to the accompanying drawings in which

Figure 1 illustrates a plant for the synthesis of dimethyl disulphide according to European patent specification 0,446,109, which may also be used according to the present invention, and

Figure 2 illustrates a plant for the synthesis of dimethyl disulphide according to European patent specification 0,446,109 and its purification to prepare dimethyl

disulphide suitable for use in the compositions of the present invention.

With reference to Figure 1 of the accompanying drawings, there is shown a plant comprising a primary reactor 1 which is a stirred reactor. The primary reactor 1 is equipped with a pipe 10 for introducing sulphur, a pipe 11 for introducing methyl mercaptan and a pipe 12 which may be used for simultaneously introducing a catalyst. The primary reactor 1 is also equipped with a pipe 13 through which gaseous effluent is removed. The primary reactor 1 is connected to a degassing system via pipe 14. The degassing system 2 is composed of a jacketed receptacle equipped with a stirrer and surmounted by a cooled column which allows methyl mercaptan, which can be carried away with the H_2S , to be recondensed before being removed. A pipe 15 allows the introduction of an inert gas into the degasser 2 and a pipe 16 allows the removal of H_2S . The degassing system 2 is connected to a finishing reactor 3 via pipe 17. A pump is placed between the outlet of the degasser 2 and the inlet of the finishing reactor 3 to allow the liquid product treated in the degasser to be fed into the reactor. The finishing reactor 3 is a stationary-bed tubular reactor which is connected to a degassing column 4 via pipe 18. The degassing column 4 is equipped with a pipe 19 for introducing inert gas and a pipe 20 for removing H_2S . Column 4 serves to completely remove H_2S dissolved in the liquid exiting from the reactor 3. The degassing column 4 is connected to a first distillation column 5 via pipe 21. The distillation column 5 separates most of the excess methyl mercaptan for recycling back to the primary reactor 1 via pipe 22. The distillation column 5 is connected to a second distillation column 6 via pipe 23. The distillation column 6 separates the residual dimethyl polysulphides (DMPS) for recycling to the finishing reactor 3 via pipe 25 or to the primary reactor 1 via pipe 26. Column 6 is also equipped with a pipe 24 at the top for collecting dimethyl disulphide.

With reference to Figure 2 of the accompanying drawings there is shown a plant as shown in Figure 1 in which pipe 24 is connected to a third distillation column 7. The distillation column 7 is equipped with a pipe 27 at the top for removing volatile impurities such as methyl mercaptan and dimethyl sulphide and a pipe 28 at the bottom for removing purified dimethyl disulphide.

In use of the above plant, sulphur is introduced into the primary

reactor 1 via pipe 10 and methyl mercaptan is introduced via pipe 11. If a catalyst is introduced simultaneously, it may be introduced via pipe 12. Gaseous effluent is removed via pipe 13. The reaction mixture at the outlet of reactor 1 is conveyed to the degasser 2 via pipe 14. H_2S , which may be eliminated by the introduction of inert gas via pipe 15, is removed via pipe 16. After treatment the mixture is conveyed via the pipe 17 to the finishing reactor 3. The mixture is then introduced via pipe 18 into the degasser 4, in order to remove H_2S via pipe 20 which has formed in the reactor 3 during the retrogression of dimethyl polysulphides by methyl mercaptan to give dimethyl disulphide. At the outlet of the degassing column 4, the mixture is introduced via the pipe 21 into the first distillation column 5, in order to remove virtually all the excess methyl mercaptan. This methyl mercaptan can then be recycled via the pipe 22 to the reactor 1. At the outlet of column 5, the mixture is conveyed via the pipe 23 into the second distillation column 6, where the dimethyl polysulphides are removed at the bottom of the column via pipe 25, in order optionally to be recycled in the reactor 3, or via pipe 26, in order optionally to be recycled in the reactor 1. The DMDS exists column 6 via pipe 24 and may be introduced into a third distillation column 7 where volatile impurities, such as methyl mercaptan and dimethyl sulphide, are removed at the column top via the pipe 27. The purified DMDS is collected at the bottom of the column via the pipe 28.

The following Examples further illustrate the invention without limiting it.

EXAMPLE 1: Synthesis of dimethyl disulphide according to the process disclosed in European patent specification 0,446,109

a) Equipment: The plant used is shown in Figure 1 as described above.

b) Procedure: Methyl mercaptan (MM) is introduced liquid into the reactor 1 under pressure via the pipe 11 with a flow rate of 960 g/h. Liquid sulphur is introduced into the reactor 1 via the pipe 10 with a flow rate of 160 g/h (MM/S = 4 molar). The reactor 1 (reaction volume: 300 ml) contains 20 g of dry Amberlyst

A21 resin. The operating pressure is maintained at 5.5 bar relative and the temperature at 40°C. The reaction mixture at the outlet of reactor 1 has the following composition by weight, excluding excess methyl mercaptan and excluding H₂S: DMDS 85%, DMPS 15%. This reaction mixture is then conveyed into the degasser 2 via the pipe 14 in order to be treated. After treatment, the mixture, freed from H₂S, is conveyed via the pipe 17 into the finishing reactor 3, which contains a charge of 94 g of dry A21 resin. The pressure in the reactor is 5.5 bar relative and the temperature 40°C. At the outlet of the reactor 3, the mixture has the following composition by weight, excluding H₂S and excluding excess methyl mercaptan: DMDS 98.5%, DMPS 1.5%. The mixture is then introduced via the pipe 18 into the degasser 4, in order to remove the H₂S which has formed in the reactor 3 during the retrogression of the dimethyl polysulphides by methyl mercaptan to give DMDS.

At the outlet of the degassing column 4, the mixture is introduced via the pipe 21 into the first distillation column 5, in order to remove virtually all the excess methyl mercaptan. This methyl mercaptan can be recycled via the pipe 22 to the introduction of the reactants into the reactor 1. At the outlet of the column 5, the mixture is conveyed via the pipe 23 into the second distillation column 6, where the DMPSs are removed at the column bottom via the pipe 25, in order optionally to be recycled in the reactor 3, or via the pipe 26, in order optionally to be recycled in the reactor 1.

The DMDS, finally collected at the top of the column 6 via the pipe 24 and known as A_o for the olfactory tests described in the following examples, has the following composition by weight:

- DMDS:	99.3%
- DMPS:	3000 ppm
- MM:	4000 ppm
- DMS:	300 ppm

EXAMPLE 2: Purification of the dimethyl disulphide prepared according to the process disclosed in European patent specification 0,446,109

The synthetic procedure is the same as that described in Example 1, except that the DMDS exiting from the column 6 via the pipe 24 is introduced into a third distillation column 7 (see Figure 2 as described above), where the volatile impurities, such as methyl mercaptan and dimethyl sulphide, are removed at the column top via the pipe 27. The DMDS collected at the column bottom via the pipe 28 has the following composition by weight:

- DMDS:	99.7%
- DMPS:	3000 ppm
- MM:	< 100 ppm
- DMS:	< 50 ppm

This purified DMDS, hereinafter known as **B₀**, and a DMDS sample **A₀** prepared in Example 1 were subjected to an olfactory test. The 8 people invited to this test unanimously recognized a marked improvement in the smell of the **B₀** DMDS in comparison with the **A₀** DMDS but everyone also reported that a garlicky and ethereal smell remained in the **B₀** DMDS.

EXAMPLE 3

2000 ppm by weight of vanillin (4-hydroxy-3-methoxybenzaldehyde) were added to 100 g of **B₀** DMDS prepared in Example 2. The complete dissolution of the vanillin was observed after one hour at 25°C. The resulting sample was known as **B₁**.

EXAMPLE 4

The vanillin used in Example 3 was replaced by 2000 ppm of ethyl vanillin (3-ethoxy-4-hydroxybenzaldehyde). Its dissolution was observed after one hour at 25°C. The resulting sample was known as **B₂**.

Examples 5 and 6 illustrate the preparation of DMDS-based compositions with the smell masked by the preferred products of the present

invention.

EXAMPLE 5

2000 ppm of a mixture composed by weight of 50% isoamyl acetate and 50% diethyl ortho-phthalate were added to 100 g of B_0 DMDS prepared in Example 2. As this mixture was liquid, dissolution was immediate at 25°C. The resulting sample was known as B_3 .

EXAMPLE 6

The mixture used in Example 5 was replaced by 2000 ppm of a mixture having the following composition by weight:

isoamyl acetate	:	25%
diethyl ortho-phthalate	:	50%
2-methylbutyl butyrate	:	15%
benzyl acetate	:	10%

The dissolution of this mixture in B_0 was immediate at 25°C. The resulting sample was known as B_4 .

The samples B_0 , B_1 , B_2 , B_3 and B_4 were subjected to a comparative of factory test carried out by the panel of 8 people mentioned in Example 2. These 8 people were asked to attribute to the samples a note ranging from 0 to 5 according to their preference with respect to the smell, the note 0 being attributed to the least preferred smell, the note 5 to the most preferred smell and the notes 1, 2, 3 and 4 allowing them to classify the intermediate levels. The results are represented in the following table:

Sample Person	B ₀	B ₁	B ₂	B ₃	B ₄
1	0	2	3	4	5
2	1	2	4	3	5
3	0	3	2	4	5
4	0	2	3	4	5
5	0	3	2	4	5
6	0	2	3	4	5
7	1	2	4	3	5
8	1	2	3	5	4
Note out of 40	3/40	18/40	24/40	31/40	39/40

It will be noted that the smell of the compositions B₁, B₂, B₃ and B₄ is always preferred to that of B₀ and that the note obtained for B₄ is very close to the maximum possible (40). The members of the panel, in addition, specified that they preferred the "fruity" note of the compositions B₃ and B₄ to the "vanilla-garlicky" note of the compositions B₁ and B₂.

Comparative Examples 7 to 11 illustrate the need to remove most of the volatile impurities from the DMDS in order to observe a significant odour-masking effect.

EXAMPLE 7

Example 3 was repeated (masking agent: vanillin) but replacing 100 g of B₀ DMDS with 100 g of the non-topped DMDS A₀ prepared in Example 1. The resulting sample was known as A₁.

The 8 members of the panel compared the smell of A₁ with that of B₀ and everyone preferred the smell of B₀ (DMDS purified of its volatile impurities and without masking agent) to that of the composition A₁ based on unpurified DMDS and on vanillin.

EXAMPLE 8

The procedure of Example 7 was followed, vanillin being replaced by

ethyl vanillin. The 8 people of the panel preferred the smell of the sample B_0 to that of the resulting sample (A_2).

EXAMPLE 9

The procedure of Example 7 was followed, vanillin being replaced by menthol. The smell of the sample B_0 was still preferred to that of the resulting sample (A_3).

EXAMPLE 10

The procedure of Example 7 was followed, vanillin being replaced by the mixture of masking products mentioned in Example 5. The resulting sample was known as A_4 . The 8 people of the panel preferred the smell of B_0 to that of A_4 .

EXAMPLE 11

The procedure of Example 7 was followed, vanillin being replaced by the mixture of masking products mentioned in Example 6. The resulting sample was known as A_5 . The smell of the sample B_0 was still preferred to that of the sample A_5 .

CLAIMS

1. A dimethyl disulphide (DMDS) composition comprising, by weight, at least 95% of dimethyl disulphide, less than 500 ppm of methyl mercaptan, less than 100 ppm of dimethyl sulphide and not more than 1% of at least one odour-masking agent.

2. A composition according to Claim 1, comprising less than 200 ppm of methyl mercaptan and less than 50 ppm of dimethyl sulphide.

3. A composition according to Claim 1 or 2, comprising 0.1 to 0.5% of odour-masking agent.

4. A composition according to any one of Claims 1 to 3, comprising approximately 0.2% of odour-masking agent.

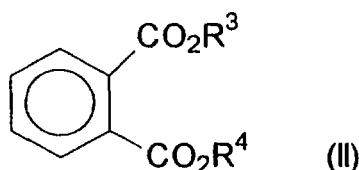
5. A composition according to any one of the preceding Claims, in which the odour-masking agent is selected from esters of general formula:



in which R^1 represents an unsaturated or saturated, linear or branched hydrocarbon-comprising radical containing from 1 to 4 carbon atoms and R^2 represents an unsaturated or saturated, linear, branched or cyclic hydrocarbon-comprising radical containing from 2 to 8 carbon atoms.

6. A composition according to Claim 5, in which the odour-making agent is selected from the group consisting of isoamyl acetate, 2-methylbutyl butyrate, isoamyl butyrate, benzyl acetate and mixtures thereof.

7. A composition according to Claim 5 or 6, in which the ester of formula (I) is used in combination with an ortho-phthalate of general formula:



in which each of R^3 and R^4 , which may be the same or different, represents an unsaturated or saturated, linear, branched or cyclic hydrocarbon-comprising radical containing from 1 to 8 carbon atoms.

5 8. A composition according to Claim 7, in which the ortho-phthalate is diethyl ortho-phthalate.

 9. A composition according to Claim 7 or 8, comprising 0.1% of isoamyl acetate and 0.1% of diethyl ortho-phthalate.

 10. A composition according to Claim 7 or 8, comprising 0.05% of isoamyl acetate, 0.03% of 2-methylbutyl butyrate, 0.02% of benzyl acetate and
10 0.1% of diethyl ortho-phthalate.

 11. Process for preparing a composition according to Claim 1, which process comprises preparing dimethyl disulphide with a reduced content of volatile impurities and adding at least one odour-masking agent, such that a dimethyl disulphide composition comprising, by weight, at least 95% of dimethyl disulphide,
15 less than 500 ppm of methyl mercaptan, less than 100 ppm of dimethyl sulphide and not more than 1% of at least one odour-masking agent is obtained.

 12. Process according to Claim 11, in which the dimethyl disulphide is prepared by distillative topping.

 13. A composition according to Claim 1, whenever prepared by
20 the process claimed in Claim 11 or 12.