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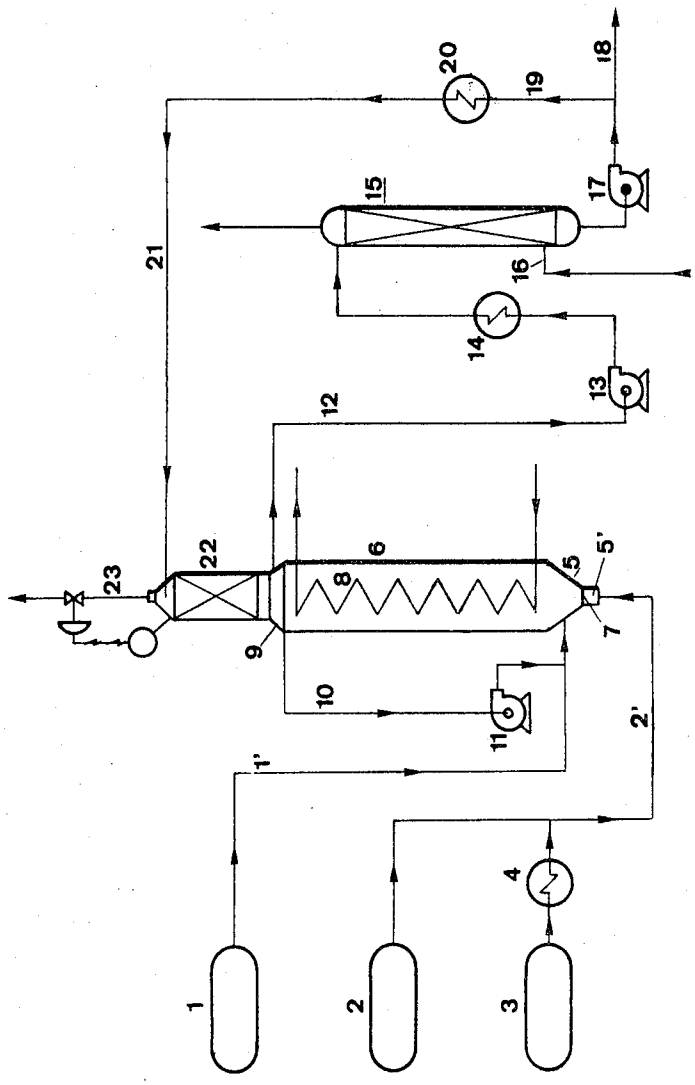

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MANUFACTURE OF DIALKYL SULPHOXIDES

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ABSTRACT OF THE DISCLOSURE

Process for the manufacture of dialkyl sulphoxides by the reaction of the corresponding dialkyl sulphide with nitrogen peroxide, in which each mole of the dialkyl sulfide reactant is diluted with from 0.15 to 3 moles of the dialkyl sulphoxide and each mole of the nitrogen peroxide reactant is diluted with from 4 to 10 moles of oxygen. In this manner increased reactant stability and improved control of the reaction is made possible.

The invention relates to an improved process for the manufacture of dialkyl sulphoxides; it is more particularly concerned with obtaining lower alkyl sulphoxides, i.e. those containing from 1 to 4 carbon atoms, and in particular dimethyl sulphoxide. The invention also comprises an installation permitting the new process to be carried into effect.

The alkyl sulphoxides and especially dimethyl sulphoxide have over the last 20 years become extremely useful products which are widely used in industry, especially as solvents and industrial processes have been developed for the preparation thereof. Unfortunately, the known methods and installations, utilising the oxidation of a dialkyl sulphide by means of nitrogen peroxide, have the serious disadvantage of involving danger of explosion. This danger is recognised by those who have worked on the question, and various solutions have been proposed.

In the known processes, the gaseous or liquid nitrogen peroxide, i.e., NO_2 and N_2O_4, reacts with liquid dialkyl sulphide in a column at a temperature between ambient temperature and approximately 80° C., and usually between 20° and 60° C. In the earliest process, described in U.S. Pat. 2,702,824, gaseous NO_2 and oxygen are introduced at the bottom of the column, while the liquid dialkyl sulphide enters at the top end thereof. In order to avoid the danger of explosion, it was proposed in French Pat. 1,271,807 that the oxidising gases should be well-dispersed within the liquid, so that the volume of gas thus retained by the liquid is at least 7% of the latter. Another process, which forms the subject of French Pat. 1,188,561, consists in using NO_2 in the form of a solution in dialkyl sulphoxide, or possibly in another solvent, and in thus introducing the solution together with the sulphide to be oxidised at the bottom of the reaction column; this process provides for the re-oxidation of the resultant NO, by contact with the oxygen in a separate reaction zone. The addition No. 73,993 to this patent provides for the treatment of the formed vapor phase, still containing dialkyl sulphide, with an excess of NO_2, before the re-oxidation of the NO, so as to avoid any presence of sulphide during this last operation. Despite all the precautions which are indicated in the prior art, the process has remained dangerous; it seems that the risks arise not only from gaseous phases capable of detonating downstream of the reaction column, but also from the apparatus in which the mixture of NO_2 and N_2O_4 with the liquid sulphoxide is prepared.

The present invention remedies the state of affairs as it exists at present: it makes possible perfect control of the oxidation of the dialkyl sulphide and higher stability in the conduct of the reaction, with elimination of all dangerous points in the manufacturing cycle. While the yield of pure sulphoxide by the new process is as good as in the best of the prior known processes, it is accompanied by the advantage of a discharging gaseous effluent which is colder and is less charged with sulphide and NO_2 than in the known processes.

The new process according to the invention for the production of a dialkyl sulphoxide by the oxidation of the corresponding dialkyl sulphide by means of nitrogen peroxide is characterised in that the dialkyl sulphide is diluted with dialkyl sulphoxide, while the nitrogen peroxide is diluted with oxygen, before the oxidation reaction.

Although the degree of dilution of the dialkyl sulphide may vary within wide limits, it is preferable that the liquid which enters the reactor is composed of 0.15 to 3 moles of dialkyl sulphoxide to 1 mole of dialkyl sulphide, or better still of 0.5 to 1.5 moles of sulphoxide to 1 mole of sulphide. In the case of manufacturing dimethyl sulphoxide, which is particularly important for practical purposes, these proportions, expressed by weight, are about 20 to 380 and preferably 60 to 190 parts of sulphoxide to 100 parts of sulphide.

On the other hand, the dilution with oxygen of the N_2O_4 intended for the oxidation is preferably such that the molar ratio O_2/N_2O_4 is about 4 to 10 or better still 5 to 8, in the gaseous mixture being used.

In the preferred form of the invention the adequate proportions of nitrogen peroxide and oxygen are injected in the form of a gaseous mixture at the bottom of a reaction column, the liquid mixture of dialkyl sulphide and dialkyl sulphoxide also being introduced into the lower part of this column. The liquid content of the reaction column is maintained in a thermal state, such that the region where the reactants are injected is at the optimum temperature for the oxidation reaction of sulphide into sulphoxide, and that, starting from this region and towards the top of the column, the temperature progressively decreases to an intermediate value between the said optimum temperature and ambient temperature.

Hence, instead of permitting the temperature to be self-established in the column, as in the prior art, possibly by heating or cooling a small lower region of the liquid (U.S. Pat. 2,702,824), the process according to the invention consists in permitting the reaction medium to become heated to the required temperature, at the point of arrival of the reactants at the bottom of the column, and in suitably cooling all the remainder of the contents of this column. In other words, according to the invention, a stable temperature gradient is created, in the sense of a decrease from the bottom towards the top of the reaction column.

In the case of the oxidation of dimethyl sulphide into oxysulphide, the preferred temperature at the point of introduction of the reactants is from 45° to 70° C. or better

still from 50° to 60° C.; the cooling of the liquid which is above this zone is then such that the temperature does not reach more than about 20° to 40° C. at the top of the column, that is to say, at the point where the liquid leaves the column.

One particularly desirable embodiment of the invention consists in dividing very finely the gases injected at the bottom of the reactor or column and in ensuring a perfectly intimate contact between them and the liquid; this can be achieved by the interposition of a plate having very fine perforations, or a porous plate, on the inlet for the gases.

The most practical procedure for the dilution of the sulphide with sulphoxide consists in that a fraction of the reaction liquid drawn off at the top of the column is introduced, together with the fresh sulphide, at the bottom of the column.

According to one particular and highly advantageous feature of the invention, the gases and vapors escaping from the top of the reaction column are washed in counter-current with the dialkyl sulphoxide produced, which is previously degasified and cooled. It is generally sufficient for this sulphoxide, thus recycled in the upper part of the column, to be at a temperature of approximately 15° to 30° C., when dimethyl sulphoxide is concerned; it can in particular be at ambient temperature, i.e. 15° to 25° C. As a general rule, the sulphoxide used for this washing operation must be at a temperature below the boiling point of the dialkyl sulphide from which it is derived. This measure, novel in relation to the prior art, permits a partial recovery of the NO_2 and dialkyl sulphide entrained by the gaseous stream; at the same time, the volume of the gaseous phase decreases, and the dangers of oxidation of the dialkyl sulphide in this phase are reduced.

In the oxidation of the dialkyl sulphide into oxysulphide, the nitrogen peroxide serves as a catalyst or intermediate oxidant and a substance taking up oxygen, in accordance with the reactions:

$$R—S—R+NO_2 \rightarrow R—SO—R+NO \quad (R=\text{alkyl})$$

$$NO+\tfrac{1}{2}O_2 \rightarrow NO_2 \quad (\text{and/or } N_2O_4)$$

Its proportion relatively to the sulphide is thus not a determining factor, but obviously it is necessary for the total quantity of NO_2 and O_2 which are present to be sufficient to oxidize all of the R—SR. In theory, 100 atoms of oxygen, i.e. 50 moles of O_2, are necessary to oxidise 100 moles of sulphide. In practice, it is desirable that, for 100 moles of sulphide, there is used a certain excess of oxidants, particularly 110 to 150 atoms of total available oxygen, or better still 120 to 130 atoms, of which about $\frac{1}{15}$ to $\frac{1}{3}$ are in the form of NO_2 and/or N_2O_4. The O_2/NO_2 molar ratio in the gaseous mixture which is employed is preferably about 4 to 10 and especially 5 to 8, as previously indicated. In other words, the proportion of nitrogen peroxide, expressed as NO_2, is generally from 5 to 20 moles and more particularly 7 to 12 moles, to 100 moles of dialkyl sulphide.

Generally, in the process according to the invention, the dialkyl sulphoxide produced experiences a degasification, that is to say, the elimination of the volatile compounds which it contains at the outlet of the reactor. For this purpose, it is reheated, usually to a temperature of the order of 60° to 80° C., and passes in counter-current in contact with air. The product thus degasified is divided into two fractions: one of which is cooled and recycled as previously indicated, while the other is neutralised and purified.

The new process is particularly adapted to continuous manufacture.

The installation according to the invention, for carrying into effect the process as described, comprises, in addition to the conventional means, one or more reactors of the column type equipped with means for introduction of gas and liquid at the lower end and cooling means acting over the entire height of the column, from a level situated above the gas and liquid inlets.

According to a preferred and highly important embodiment, the bottom region of the column where the gases enter is separated from the remainder of the internal space of the column by a plate perforated with a large number of very small apertures; such a plate can with advantage be formed of a sintered metal; it permits an excellent distribution of the gases, NO_2 and oxygen, and of the liquid dialkyl sulphide introduced at the bottom of the column, as they flow upwardly.

The reaction column according to the invention is generally equipped with means for the recirculation of the liquid from the top of the column towards the inlet at the bottom of the latter. Quite obviously, it comprises an outlet for unrefined manufactured product in its upper part.

In one preferred form of the invention, the reaction column is surmounted by a scrubbing column, generally lined with filler bodies, in which the gaseous effluent leaving the reaction medium is scrubbed and cooled by sprinkling with suitably cooled, recycled reaction product. By inference, the new installation comprises cooling means in the initial sulphoxide circuit and on a branch line of a fraction of produced sulphoxide.

In general, the installation also comprises means for degasifying the manufactured product, these means comprising one or more reheaters. The cooling means referred to above are preferably arranged on a branch line of the manufactured product and are downstream of the degasifying means.

An installation and the manufacture of dimethyl sulphoxide, starting with dimethyl sulphide, will now be described as a non-limiting example.

The accompanying drawing illustrates diagrammatically the installation which is used. In this diagram, **1** represents a source of liquid dimethyl sulphide, **2** is an oxygen gas reservoir and **3** is a source of liquid NO_2. Represented at **4** is an NO_2 vaporiser. By way of a conduit **1'**, the dimethyl sulphide is brought in liquid form to the lower part **5** of a reactor, in the form of a column **5–6**. The oxygen and the nitrogen peroxide, in the form of a gaseous mixture, also reach the bottom **5** of the reactor through the pipeline **2'**.

The conical portion **5** is terminated at the bottom by a small sleeve **5'** at which ends the gas supply pipe **2'** ends; the interior of the sleeve **5'** is separated from the interior **5** by a porous plate **7** made of sintered metal, which serves for the fine distribution of the gases in the liquid which is above the plate **7**.

Installed in the body **6** of the reactor are one or more coolers **8** serving to cause the progressive lowering of the temperature of the reaction medium to a value which is relatively close to ambient temperature, below the region **9** at the top of the column.

Connected to the upper part of the column **5–6** is a discharge conduit **10** comprising a recirculating pump **11**, for sending a part of the liquid into conduit **1'** through which the fresh dimethyl sulphide reaches the bottom **5** of the column.

Connected to the top of the section **9**, filled with Raschig rings, is the discharge pipe **12** for unrefined sulphoxide which is produced. This sulphoxide is taken up by a pump **13**, directed into a reheater **14** and is passed to the top of a degasifying tower **15**, through which flows an air current introduced through the bottom at **16**. The sulphoxide taken up by the pump **17** is divided into two fractions, one passing by way of **18** towards the conventional apparatus for neutralisation and purification purposes, and the other by way of **19**, through a cooler **20**, and is recycled through the pipeline **21** to the top of the scrubber **22** which is arranged above the section **9** of the reactor **5–6**. The scrubber **22** contains filler bodies, particularly Raschig

rings, and/or plates. The gaseous effluent leaves the apparatus through **23**.

By way of example, there are given here the operating conditions for the manufacture of dimethyl sulphoxide at the rate of 3 tons per day, using the installation according to the diagram which has been described.

Supply of:		
Dimethyl sulphide	kg./h.	125
Oxygen	$m.^3/h.$	*23.5
Liquid NO_2	kg./h.	8.0
Produced crude sulphoxide	kg./h.	141.5
Recycled sulphoxide	kg./h.	140.0
Gaseous effluent	$m.^3/h.$	*5.0
Temperature at:		
Bottom of reactor (at **5**)	° C.	52
Middle of reactor (at **6**)	° C.	42
Top of reactor (top of **6**)	° C.	38
Temperature of gaseous effluent (at **23**)	° C.	20
Pressure above ambient pressure	$kg./cm.^2$	0.6
Yield of pure sulphoxide	percent	90

*At n.t.p.

It is to be noted that, in a conventional installation, in which NO_2 is introduced in the liquid state admixed with sulphoxide at the bottom of the column, the latter not comprising either a porous plate or a condenser, or a trickling-type scrubber at the top (and hence no recycling of the sulphoxide), and for the same production and with the same yield, there was a gaseous effluent of 6 $m.^3$, that is to say, 20% more, and this effluent left at a temperature of 35° C. instead of 20° C. The pressure of this conventional installation was 0.4 $kg./cm.^2$ and the distribution of the temperatures in the reactor was 58° C. at the bottom, 62° C. in the middle and 61° C. at top. It is seen that, contrary to the invention, the temperature was at its maximum in the middle and higher at the top than at the bottom. It is to be noted that the operaional procedure was difficult to regulate in this conventional installation, whereas the operation of the installation according to the invention was very simple.

What is claimed is:

1. A process for the manufacture of a dialkyl sulphoxide by oxidation of the corresponding liquid dialkyl sulphide which comprises injecting said dialkyl sulphide, mixed with said dialkyl sulphoxide, and a gaseous mixture of oxygen and nitrogen peroxide into the bottom of a reaction column having a stable temperature gradient established over the entire column, said temperature gradient being such that the bottom of said column is maintained at the optimum temperature for the oxidation reaction of the sulphide and the temperature progressively decreases to an intermediate value between said optimum temperature and room temperature at the top of said column.

2. The process of claim **1** wherein said sulphide is dimethyl sulphide, the optimum temperature at the bottom of the column is from 45°–70° C., and the temperature at the top of the column is not more than about 20°–40° C.

3. The process of claim **1** wherein the sulphoxide mixed with the sulphide before the oxidation reaction is used in the form of a liquid fraction obtained after the oxidation reaction.

4. The process of claim **1** wherein the proportion of nitrogen peroxide, expressed as NO_2, is from 5 to 20 moles per 100 moles of said dialkyl sulphide.

5. The process of claim **4** wherein the gases and vapor from the top of the reaction column are scrubbed in countercurrent with dialkyl sulphoxide which was produced in said oxidation and which has been degasified and cooled to a temperature from 15°–30° C.

6. The process of claim **1** wherein the mixture of sulphoxide and sulphide injected in the bottom of the reaction column contains 0.15 to 3 moles of dialkyl sulphoxide per 1 mole of dialkyl sulphide, the molar ratio of oxygen to nitrogen peroxide in the gaseous mixture thereof is about 4 to 10, and the proportion of nitrogen peroxide, expressed as NO_2, is from 5 to 20 moles per 100 moles of dialkyl sulphide.

7. The process of claim **1** which consists essentially of employing a mixture containing 0.5 to 1.5 moles of dimethyl sulphoxide per 1 mole of dimethyl sulphide, a molar ratio of oxygen to nitrogen peroxide in the gaseous mixture thereof of 5 to 8, employing nitrogen peroxide, expressed as NO_2, in a proportion of 7 to 12 moles per 100 moles of dimethyl sulphide and maintaining the temperature in the bottom of said reaction column at from 50°–60° C.

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