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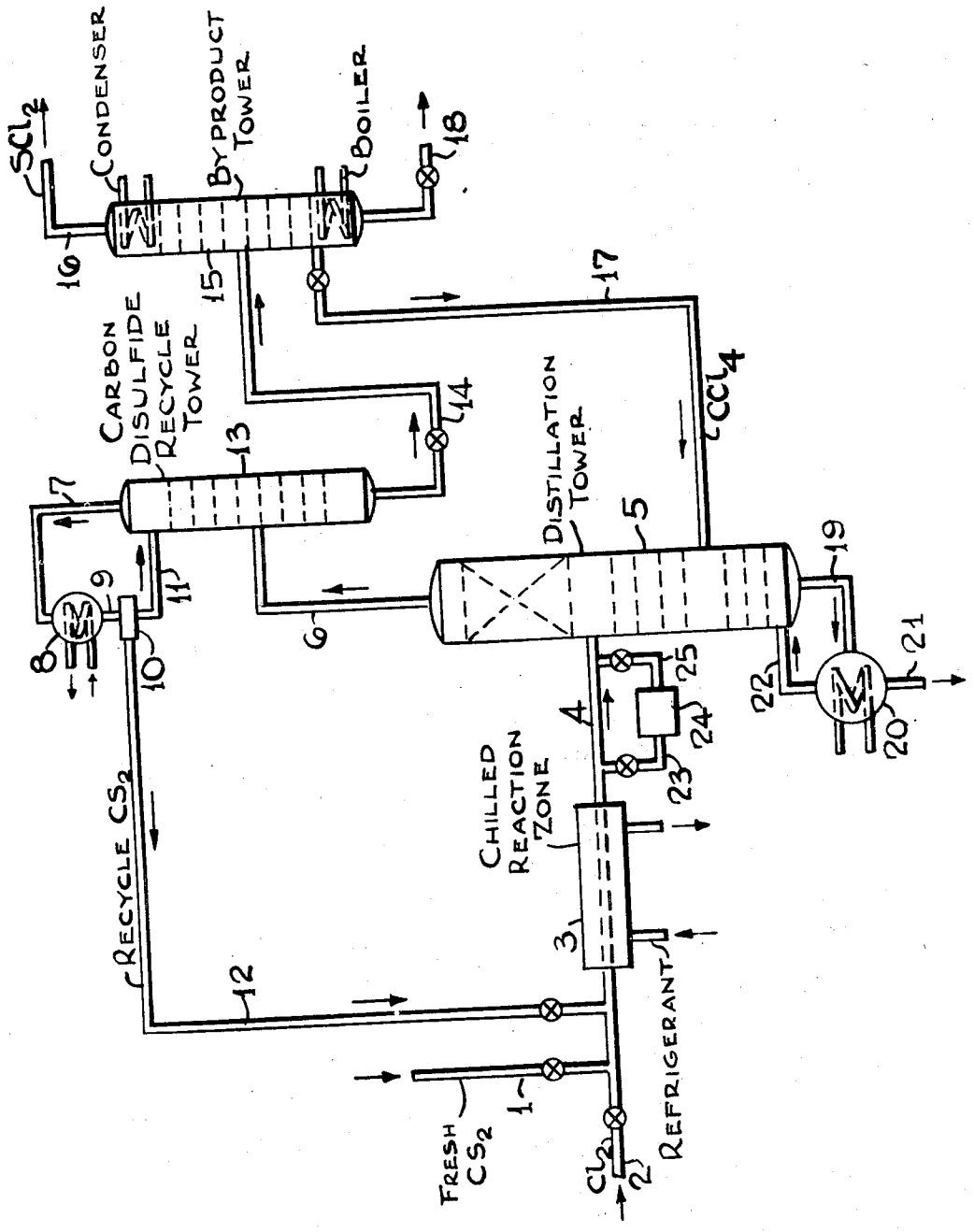

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CONTINUOUS PROCESS FOR MANUFACTURE OF PERCHLOROMETHYL MERCAPTAN

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1

This invention relates to an improved process for the preparation of perchloromethyl mercaptan.

Perchloromethyl mercaptan is an important intermediary in the manufacture of lube oil additives and parasiticides. It is conventionally prepared in a batch process employing stoichiometric amounts of carbon disulfide and chlorine as indicated in Equation 1:

(1) $2SC_2+5Cl_2 \rightarrow 2CCl_3-S-Cl+S_2Cl_2$

This process suffers from several disadvantages. The boiling point of S_2Cl_2 is 137° C., which is close to that of perchloromethyl mercaptan which boils in the range of 142°–149° C. and hence it is usually necessary to separate the two by steam distillation. Steam hydrolyzes S_2Cl_2 in the manner shown in Equation 2:

(2) $2S_2Cl_2+2H_2O \rightarrow SO_2+3S+4HCl$

The products of Equation 2 are highly corrosive and contain, in addition, finely-divided sulfur, making it a very difficult mixture to handle on a large scale basis. Some of the sulfur liberated is in the vapor phase which results in clogging and fouling of equipment.

In addition, during the course of the reaction, some carbon disulfide reacts as indicated in Equation 3:

(3) $CS_2+3Cl_2 \rightarrow CCl_4+S_2Cl_2$

This results in an undesirable production of carbon tetrachloride and a reduction in the selectivity in the direction of the production of the perchloromethyl mercaptan. This reaction, of course, also produces additional S_2Cl_2, from which the perchloromethyl mercaptan has to be separated.

The present invention provides a method for obtaining perchloromethyl mercaptan relatively free of S_2Cl_2. The improved method comprises conducting the reaction in a continuous manner so that formation of SCl_2 rather than S_2Cl_2 is favored, and also rapidly removing the SCl_2 and other reactive materials from the perchloromethyl mercaptan under relatively non-reactive conditions so that undesirable degradation and reduction in yields of the perchloromethyl mercaptan are avoided.

SCl_2 boils at a temperature of 59° C. and in the process of this invention wherein its reactivity is minimized, it can be readily separated from perchloromethyl mercaptan which boils at a temperature of at least 83° C. higher. For convenience, the boiling points of the normally

2

liquid materials encountered in the process of this invention are listed below in Table I:

Table I

	Boiling points
CS_2	46° C.
SCl_2	59° C.
CCl_4	77° C.
S_2Cl_2	137° C.
Perchloromethyl mercaptan	142°–149° C.

At low temperatures, i. e., below 25° C., and preferably temperatures in the range of 0°–15° C., the reaction proceeds according to the process of this invention in the manner indicated in Equation 4:

(4) $CS_2+3Cl_2 \rightarrow CCl_3-S-Cl+SCl_2$

SCl_2 is a powerful chlorinating agent, however, as indicated by Equation 5:

(5) $2SCl_2 \rightarrow S_2Cl_2+Cl_2$

The mechanism of Equation 5 is capable of reducing the selectivity to perchloromethyl mercaptan by the undesirable reaction of Equation 3 above. The maintenance of the reaction zone within the temperature range of this invention prevents to a substantial extent these latter two reactions (Equations 5 and 3).

Another difficulty overcome in the process of this invention is the reaction indicated in Equation 6:

(6) $CCl_3-S-Cl+SCl_2 \rightarrow CCl_4+S_2Cl_2$

The reaction of Equation 6 would also diminish the yields of desired production.

Thus the undesirable side and degradation reactions which prevent the reaction from proceeding in the manner indicated by Equation 4 are greatly diminished by cooling the exothermic reaction to the temperature range indicated. In addition, according to the process of this invention the perchloromethyl mercaptan product formed is subsequently rapidly separated from other reactive products under conditions which also minimize these undesirable reactions such as Equation 6 which result in product losses.

It has also been found that the presence of excess carbon disulfide over the stoichiometric amount required in Equation 4 tends to increase the selectivity of the reaction in the direction of perchloromethyl mercaptan by the reaction of Equation 4 as compared to the undesired production of carbon tetrachloride. The preferred excess of carbon disulfide is in the range of 20%–100%. The actual molar quantities prefer-

entially employed are in the range of 1⅕ mols to 2 mols of carbon disulfide to each 3 mols of chlorine. This phenomenon of increased selectivity is probably due to the depression of the chlorine partial pressure by the presence of excess carbon disulfide. This excess of CS_2 represents a margin of safety, as an excess of only 16% chlorine over the indicated stoichiometrical amount is sufficient to convert all the perchloromethyl mercaptan to carbon tetrachloride if allowed to react.

In order to remove SCl_2 from the reaction zone, at low temperatures for the reasons discussed above, a vacuum distillation may be used. The process of this invention preferably accomplishes the removal of the SCl_2 at low temperatures in the presence of excess CCl_4 vapors accumulated in the process which serve as an inert atmosphere and prevent the beforementioned degradation reactions.

Auxiliary inert gas stripping agents may be employed in the distillation of the CCl_4 and more volatile materials from the perchloromethyl mercaptan. Thus CO_2, N_2 and other gases boiling below about 100° C. may be used. Water is not desirable for use as it hydrolyzes the SCl_2. The use of the indicated stripping agents increases equipment size needs, however, and also renders the condensation of the desired volatile products more difficult. The use of stripping agents may consequently be dispensed with.

The selectivity obtained by the process of this invention, i. e., utilizing the indicated temperatures, excess carbon disulfide and rapid removal of reactive materials, results in selectivities of 90% as compared to 60% selectivities obtained by the prior art (Gilman and Blatt, "Organic Synthesis, Coll. vol. I, page 506).

This invention will be better understood by reference to the flow diagram shown in the drawing.

In the system shown, fresh carbon disulfide enters the chilled reaction zone 3 through lines 1 and 2. Chlorine enters the reaction zone 3 through line 2. The mixture is agitated strongly and is cooled to a temperature of 0°–15° C. The reaction mixture, after a period of 1 to 15 minutes, is withdrawn through line 4 to a distillation tower 5, which is maintained at atmospheric or subatmospheric pressures.

Warm CCl_4 vapors which enter the tower 5 below the feed point through line 17 heat the predominantly liquid mixture to its boiling point and carbon tetrachloride and the reactant mixture of SCl_2, CS_2, and traces of chlorine, are rapidly taken overhead through line 6 to tower 13. Some CCl_4 condenses in tower 5 and flows down the tower as a liquid with the perchloromethyl mercaptan. The liquid mixture leaves tower 5 through line 19 and enters reboiler 20. The CCl_4 is vaporized and returned to tower 5 through line 22. The remaining liquid consisting predominantly of perchloromethyl mercaptan is withdrawn through line 21.

Operation of tower 5 in the manner indicated also prevents the development of excessive temperatures at localized areas which would result in product decomposition and degradation. While the CCl_4 vapor stream has been shown entering the tower below the feed point through line 17, it may also enter at other points and still achieve the desired results.

In distillation tower 13 the carbon disulfide is rapidly taken overhead through line 7, cooled and condensed in condenser 8, and passed through

line 9 into drum 10. A portion of the carbon disulfide condensate containing dissolved traces of chlorine is recycled through line 12 to line 2 and reaction zone 3. The residual portion of the condensate in drum 10 is refluxed through line 11 to tower 13.

The liquid mixture of predominantly carbon tetrachloride and SCl_2 is withdrawn through line 14 to distillation tower 15, which is maintained at atmospheric or slightly subatmospheric pressure. The liquids in tower 15 no longer constitute a reactive system. It is desirable, however, to conduct this distillation rapidly to prevent SCl_2 decomposition. The SCl_2 is taken overhead through line 16. The major portion of the carbon tetrachloride may be withdrawn as a vapor from a lower portion of tower 15 through line 17 to distillation tower 5. The carbon tetrachloride vapors thus serve as the heating agent in tower 5. Sufficient liquid carbon tetrachloride to prevent buildup in the system is withdrawn through line 18.

The chlorine may enter reaction zone 3 through a plurality of points rather than at one point as described.

The reaction zone is maintained at approximately atmospheric pressure or higher. Since the chlorine is maintained largely in the liquid phase because of its solubility, there is no need for going to very high pressures.

The reaction mixture may be withdrawn from the reaction zone after the early period of reaction, i. e., 15 minutes, to a holding zone, cooling drum 24 through line 23. Most of the exothermic heat of reaction is evolved during this early period. Use of an auxiliary cooling drum permits of lesser refrigeration and agitation in this equipment while the temperature is maintained in the desired range, and permits the reaction to proceed further to completion. The mixture is then sent to the tower 5 through lines 25 and 4.

The perchloromethyl mercaptan withdrawn through line 21 is relatively free from S_2Cl_2 and may be used as is, or further purified by means such as, for example, mild alkaline scrubbing, vacuum or ordinary distillation.

Catalysts known in the art for chlorination, such as iodine, ferric chloride, and aluminum chloride, are desirably utilized in the reaction and can be removed from the products if desired by standard procedures, such as by washing with an aqueous medium, vacuum or ordinary distillation, filtration, treating with mild reducing agents such as thiosulfate, etc. The reactor stripping tower and distillation equipment may preferably be glass, glass-lined steel and other material relatively inert to chlorine and perchloromethyl mercaptan such as the noble metals and tantalum or alloys such as Hastelloy.

The process of this invention is illustrated in the following examples.

Example I

A reaction product mixture of the following proportion of starting materials, 1 mole of CS_2 to 3.1 moles of Cl_2, catalyzed by iodine, was distilled in the ordinary manner at atmospheric pressure. The chlorine figure represents chlorine actually absorbed and taken up by the CS_2. The products obtained were 40 vol. per cent S_2Cl_2, 53 vol. per cent CCl_4 and 7 vol. per cent SCl_2 with no perchloromethyl mercaptan. The latter had apparently all undesirably been converted to CCl_4.

Example II

A series of runs were made in which the ratio of chlorine to CS_2 was varied from 0.5 mole of Cl_2/mole CS_2 to 2.5 moles Cl_2/mole CS_2. The latter ratio represents the maximum at which the excellent selectivities given above can be obtained. The following run was made with the chlorine concentration at the upper end of the desired level.

A reaction product mixture of the following proportion of starting materials, 1 mole of CS_2 to 2.4 moles of Cl_2, catalyzed by iodine, was distilled in the manner of this invention. The chlorine figure represents chlorine actually absorbed and taken up by the CS_2. The products obtained were 48 vol. per cent perchloromethyl mercaptan (98% pure, only little S_2Cl_2), 7 vol. per cent CCl_4, 37 vol. per cent SCl_2 and 8 vol. per cent CS_2.

This illustrates the necessity of the rapid removal of the SCl_2 from the reaction zone at lower temperatures than ordinary atmospheric distillation and the desirability of keeping the concentration of reactants within the preferred range.

Another advantage of the process of this invention resides in the recovery of the SCl_2 which is a valuable by-product.

It is to be understood that the invention is not limited to the specific examples which have been offered merely as illustrations and that modifications may be made without departing from the spirit of the invention.

What is claimed is:

1. A process for the continuous preparation of perchloromethyl mercaptan which comprises the steps of reacting carbon disulfide and chlorine in a reaction zone at a temperature in the range of 0°–15° C., the carbon disulfide being present in an amount of 1⅕ mole to 2 moles per 3 moles of chlorine; withdrawing the resulting predominantly liquid reaction mixture to a first distillation zone; quickly removing at subatmospheric pressure from said first distillation zone a vaporous mixture of carbon tetrachloride, SCl_2, carbon disulfide, and traces of chlorine; rapidly separating the carbon disulfide and chlorine from the vaporous mixture taken off from the first distillation zone in a second distillation zone; cooling and condensing effluent vapors from the second distillation zone to form a carbon disulfide condensate containing some dissolved chlorine; recycling a portion of said carbon disulfide condensate to the reaction zone; refluxing a residual portion of the condensate to the second distillation zone; withdrawing a liquid bottoms mixture comprising predominantly carbon tetrachloride and SCl_2 from the second distillation zone to a third distillation zone; rapidly distilling the SCl_2 from the third distillation zone; withdrawing carbon tetrachloride as a bottoms liquid from the third distillation zone; withdrawing a carbon tetrachloride vapor stream from said bottoms liquid of the third distillation zone; recycling this carbon tetrachloride vapor stream to the first distillation zone; and removing perchloromethyl mercaptan as bottoms from the first distillation zone.

2. A process as in claim 1 in which the carbon tetrachloride vapor stream is returned to the first distillation zone at a point below the feed point.

3. A process as in claim 2 in which the withdrawn liquid bottoms from the distillation zone is reboiled to vaporize any carbon tetrachloride contained therein and the thus vaporized carbon tetrachloride is returned to the distillation zone.

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