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PROCESS FOR PRODUCTION OF ALKYL MERCAPTANS

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Our invention relates more particularly to a process for production of alkyl mercaptans by reaction of the corresponding alkyl chloride with sodium hydrosulphide, in accordance with the following reaction:

$$RCl+NaHS \rightarrow RSH+NaCl$$

in which R may be any alkyl radical of the group herein defined.

It is known that alkyl chlorides may be reacted with an alkali metal hydrosulphide in methyl or ethyl alcohol, at 125° to 150° C., and under substantial pressure. Some of the alkyl chloride is hydrolyzed to the alcohol and some of it is dehydrochlorinated to the olefin. A considerable quantity of dialkyl sulphide is formed. The alcohol must be recovered from the aqueous phase.

It is also known that decyl to pentadecyl chlorides may be reacted with potassium hydrosulphide in a medium of butanol, at atmospheric pressure, by refluxing the reagents together. This process is open to the serious objection that KHS is not a commercial product and must therefore be formed in situ in the butanol by reaction of H_2S with KOH, a process which is simple enough if performed in glass on a laboratory scale, but difficult on a plant scale. For each mol of KHS one mol of H_2O is formed, but the quantity of butanol used is such that the proportion of water to butanol is within the limit of its solubility in the reaction mixture. The reaction is therefore performed in a single-phase medium. Nevertheless, the yield of mercaptan in this process is very low, a large proportion of the product consisting of the dialkyl sulphide.

One object of our process is to make possible the use of sodium hydrosulphide in place of potassium hydrosulphide, and in particular the use of commercial flake sodium hydrosulphide, containing water of crystallization, without involving super atmospheric pressure or recovery of alcohol from an aqueous medium.

Another object of the invention is to avoid the complications involved in refluxing. Still another object of the invention is to improve the yield by minimizing production of the dialkyl sulphides. A further object is to improve the quality of the product by preventing decomposition and by the removal of colloidal impurities.

We have now found that by the aid of mechanical agitation, and without refluxing, alkyl chlorides can be reacted with sodium hydrosulphide in a two-phase medium, one phase comprising a water solution of the hydrosulphide, the other phase comprising a solution of the alkyl chloride

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in a solvent with which the water solution of hydrosulphide has a limited miscibility, and which boils preferably above the reaction temperature and below the boiling point of the mercaptan. This permits of the use of relatively cheap commercial flake NaHS, containing water of crystallization, in place of NaHS or KHS formed in the reaction mixture, and affords the further very practical advantage that the reaction can be carried out in an iron reactor.

As a typical example of our process, we will describe production of a mixture consisting of decyl to octadecyl mercaptan inclusive, from the corresponding chlorides, obtainable by treatment of the mixture of alcohols known by the trade name of "Lorol," which is derived from cocoanut oil. This mixture of mercaptans will hereafter be referred to as "Lorol mercaptan" and the chlorides from which it is produced as "Lorol chloride."

"Lorol" chloride will not react to any practicable extent with solutions of sodium hydrosulphide in water alone or in methyl or ethyl alcohol solutions at temperatures attainable at ordinary pressures, even with vigorous agitation. We have found, however, that with mechanical agitation Lorol chloride can be made to react very completely with sodium hydrosulphide at atmospheric pressure and at a temperature below its refluxing temperature in a two-phase medium comprising a water solution of the hydrosulphide and a solvent for the Lorol chloride with which the water solution has a limited miscibility, such as butanol. For this purpose we mix the NaHS in flake form, containing 30 per cent water of crystallization, or 43 per cent water, based on hydrosulphide, with butanol, which may have been recycled from a previous cycle of the process and may contain up to 10 per cent water, in the typical proportions of 970 lbs. of NaHS to 1,500 lbs. of butanol. We heat these materials to from 70° to 110° C. and agitate them thoroughly together. This causes the NaHS to dissolve largely in its water of crystallization and results in formation of two distinct liquid phases, the aqueous phase containing most of the NaHS and the butanol a small part of the NaHS or NaHS solution mixed therewith or dissolved therein. We preferably pass in H_2S until both phases are thoroughly saturated therewith and excess H_2S bubbles through the mixture. We then charge in 1,700 lbs. of Lorol chloride at room temperature, with stirring. This is about two-thirds of the molecular equivalent of the NaHS. The addition of the Lorol chloride having cooled the mixture, we heat it again and agitate it, preferably while continuing to pass in H_2S, until the reaction is substantially complete with respect to the Lorol chloride, about one-third of the hydrosulphide remaining unreacted. During the reaction the temperature is held at 100° C. After about one hour, the supply of H_2S may be diminished.

Although the NaHS used is practically free from Na_2S, NaHS has a tendency to give up H_2S and form Na_2S, which then reacts with the alkyl chloride to form the unwanted dialkyl sulphide. The latter may also be formed directly, or by loss of H_2S from two molecules of the mercaptan. Saturation of the alcohol medium containing NaHS with H_2S before addition of the Lorol chloride and addition of H_2S to the reaction mixture during the reaction, and in particular addition of a very great excess during the first hour, are therefore very important, and have been found to increase the mol ratio of mercaptan to dialkyl sulphide in the product substantially.

The time required for the reaction depends upon the temperature and the vigor of the agitation. Our process, as ordinarily conducted, starting at 85° C. and finishing at 100° C., requires eight hours. The product contains less than one per cent of chlorine. By using a greater excess of NaHS or continuing the process longer, the residual chlorine can be cut down still lower.

It should be noted that in our process the water present during the reaction is that which is introduced with the flake NaHS and butanol. This amounts to 7 to 15 per cent of the total weight of the reaction mixture. Any water in excess of this proportion is a hindrance.

It should also be noted that the butanol is not a mutual solvent for the reagents, in the ordinary sense, since the solubility of NaHS of NaHS solution in butanol is slight and miscibility of water therewith limited. Nevertheless, we believe that it is the NaHS in the butanol that reacts with the Lorol chloride, and that this is replenished, as fast as used up, by NaHS from the aqueous layer.

After completion of the reaction in the manner above described, the NaCl produced as a by-product adheres to the sides and bottom of the reactor. To remove this we add water and agitate. The lower aqueous phase containing NaCl and excess NaHS is then drawn off. The organic phase, comprising the butanol, product and any unreacted Lorol chloride, is then washed with strong brine solution. This breaks down certain highly objectionable colloidal impurities formed in the product. Acidifying with an acid, such as HCl, is also effective in breaking down the colloidal impurities. We believe that the breaking down of these impurities is an electrochemical effect and that any strong aqueous salt or acid solution, acting as an electrolyte, will serve the same purpose. After the impurities have been modified in this way they cease to be troublesome. We then draw off the aqueous phase again, and distill off the butanol from the crude mercaptan for reuse. The weight of crude mercaptan is approximately equal to the weight of Lorol chloride used. Finally we fractionate the product. In this latter step any di-Lorol sulphide is left behind, as well as any other high boiling impurities. The distilled mercaptan boils typically at 120° to 186° C. at 5 m. m. and contains about 0.35 per cent chlorine and 14.3 per cent sulphur combined as SH, or mercaptan sulphur.

The finished product is much more uniform and lower in impurities than that of the prior art, obtained by reaction under pressure in a medium of methyl or ethyl alcohol. It is also comparatively free from the decomposition products of the prior art. Our product has on this account been found very superior for use in the reactions requiring a uniform high grade material.

In the process of the prior art in which a water miscible solvent is used, the recovery of the solvent from the aqueous phase constitutes an additional expense. In our process, the organic phase, containing the butanol and product, forms a layer so distinct that the aqueous phase may be drawn off without difficulty. The latter contains less than 4 per cent butanol and no recovery of the butanol from the aqueous phase is necessary.

In our process the choice of an organic solvent is determined by the considerations that it must be miscible with the alkyl chloride and the water solution of hydrosulphide must be slightly miscible with it, yet not so miscible as to result in a single phase system or require a distillation to separate it from the wash water; also the organic solvent should preferably boil above the preferred reaction temperature, to avoid the necessity for refluxing or pressure, but substantially below the mercaptan, to facilitate recovery of the product from the solvent. These properties are possessed or lacking in varying degrees by the alcohols used in the following series of experiments:

1	2	3	4	5	6	7	8
Alcohol used as medium	Temp. of reaction	NaHS in alcohol phase [1] g. p. l.	NaHS in reaction mixture g. p. l. after—		Per cent chlorine reacted in 6 hrs.	Per cent chlorine replaced by SH	Yield of mercaptan in 6 hrs.
			½ hr.	6 hrs.			
n-Butanol	97–98	17.40	2.7	13.00	96.2	83	88
Isopropanol	82–84	57.10	3.15	4.80	89.7	55	54
Isobutanol	97–98	14.10	1.30	1.75	80.0	78	68
Active amyl	97–98	8.75	0.54	0.91	55.5	76	46
"Lorol"	97–98	8.50	0.61	0.45	38.7	60	25
Geraniol	97–98	5.30	--------	0.67	31.0	63	21

[1] After addition of flake NaSH, but before addition of Lorol chloride.

All the above experiments were carried out under comparable conditions, and with reagents in the same proportions, which are those used in our preferred process. In a flask provided with an agitator were placed 180 grams of the alcohol, 10 grams of water, and 120 grams of 70% flake NaSH. The temperature was raised to 85° C., with stirring, and held there for a half hour. In all cases two liquid layers were formed, the shallow lower layer containing most of the hydrosulphide and water. From the upper alcohol layer a small sample was drawn off and analyzed for NaHS, giving the values shown in column 3, which represent the solubility of NaHS solution in the organic layer under the conditions of the reaction. The mixture was then saturated with H_2S and 205 grams of Lorol chloride were added.

During the ensuing reaction, the mixture was agitated vigorously, at the temperature indicated in the table, while a current of H_2S was bubbled through it. The temperature was necessarily lower in the case of the isopropanol, because of its lower boiling point. In all cases a two-phase system formed and after one-half hour and a brief settling the organic phase was sampled and analyzed for dissolved NaHS, giving the values shown in column 4. The reaction was continued for 6 hours, and the same phase was analyzed again for NaHS, giving the values shown in column 5. The organic phase of the reaction mixture was then analyzed for chlorine and the percentage of the chlorine that had been reacted out calculated. The results are given in column 6. The mixture was also analyzed for sulphur combined as SH, or mercaptan sulphur, to show what proportion of the chlorine reacted out had been replaced by an SH group, i. e., the efficiency of conversion of the Lorol chloride to Lorol mercaptan, as distinguished from di-Lorol sulphide. These results are shown in column 7. It is not possible to express the yield of mercaptan as a percentage of the theoretical yield, as the average molecular weight of the mixture of mercaptans making up Lorol mercaptan is not precisely known, hence the theoretical yield cannot be exactly calculated. However, it can be assumed that the molecular weight of Lorol mercaptan is nearly the same as that of Lorol chloride. On this assumption the yield of mercaptan was calculated from the mercaptan sulphur. Hence in column 8 the yield of mercaptan is arbitrarily given as a percentage of the Lorol chloride used.

These results constitute conclusive evidence that in our process the mercaptan is produced by a mechanism differing entirely from that of the simple one-phase system of the prior art. In all cases the alcohol used was miscible with Lorol chloride, to form the upper organic phase of the reaction mixture. At no time however did this phase contain more than a small proportion of the NaHS, which was continually reacting with Lorol chloride to form the mercaptan, and being replenished by agitation in contact with the lower aqueous phase containing the large excess of NaHS. The reaction with Lorol chloride was so rapid that when a sample was taken out at the end of the first half hour, the reaction continued and used up some of the NaHS content before the analysis could be completed. At the end of the 6 hour period the reaction had slowed down and analysis then gave the true concentration of NaHS in the organic phase. For this reason the figures in column 5 are higher than in column 4, and more reliable.

The higher the sustained concentration of NaHS in the organic phase after the reaction has proceeded for a time, the faster the reaction should take place. By arbitrarily limiting the reaction time to 6 hours, we have shown that this is the case. The extent of the reaction, as indicated by the lowering of the chlorine content and increase of the mercaptan sulphur content, as well as the yield of the mercaptan, is a function of the concentration of NaHS in the organic phase of the reaction mixture.

The characteristics which the solvent should have in order to be useful in our process may be summarized as follows:

1. The solubility of the solvent in the water and brine used for washing the product should preferably be so low that recovery of alcohol from the wash water may be dispensed with. This is notably true of the n-butanol, but not of isopropanol, as 95% of the latter solvent is carried away in the washes, necessitating a recovery of the alcohol.

2. The solvent should not promote formation of di-Lorol sulphide. With n-butanol, 83% of the chlorine reacted out is replaced by the SH or mercaptan group. Isopropanol, on the other hand, promotes the formation of di-Lorol sulphide to such an extent that only 55% of the chlorine reacted out is replaced by SH, as shown in column 7.

3. The boiling point of the solvent should be high enough to permit an adequate reaction temperature, without the use of pressure. This is true of all the alcohols used in the above series except isopropanol, which is unsatisfactory in this respect, as unless pressure is used it permits of a reaction temperature of not over 82–84° C., whereas a temperature of 97–98° C. is desirable.

4. The boiling point of the solvent should be sufficiently below that of the mercaptan to allow the solvent to be easily separated from it by vacuum distillation. "Lorol" and geraniol are unsatisfactory in this respect because their boiling points lie too close to that of the crude mercaptan.

For these reasons, such solvents as isopropanol, Lorol and geraniol are not considered practical for our process. These solvents were included in the table to emphasize the particular advantages of the other solvents, especially of n-butanol.

It is of interest to note that the presence of the product affects the solubility of the hydrosulphide in some of the alcohols much more than in others, and that affects the speed of the reaction. Hence the reaction requires much more time in some alcohols than in others. In this respect again n-butanol appears much superior to the other alcohols for our purpose.

Although butanol has been used before for the reaction of dodecyl and tetradecyl chlorides and bromides with KHS in a single-phase medium, it appears to be inferior for this purpose to ethyl alcohol. The discovery that n-butanol has peculiar advantages in our type of two-phase reaction is therefore believed to be new and important.

We do not wish, however, to be limited to the above mentioned alcohols as solvents for use in our process, as other solvents have been found suitable for our purpose, such as those known by the trade name of "Cellosolve," which are ether alcohols.

Since Lorol chloride includes the chlorides from decyl to octadecyl, it is obvious that our process is applicable to any individual chloride of this series. For example, we have produced cetyl mercaptan from cetyl chloride by our process. However, our process is not limited to mercaptans of 10 to 18 carbon atoms, but is applicable to mercaptans of a somewhat wider range, namely those of 8 to 20 carbon atoms.

We claim as our invention:

1. The process for production of alkyl mercaptans of 10 to 18 carbon atoms by reaction of the corresponding alkyl chloride with sodium hydrosulphide in a two-phase system which comprises agitating the hydrosulphide at 70° to 100° C. with water amounting to not less than substantially 43 per cent of the weight thereof, and an alcohol boiling above 85° C. but below the boiling point

of the mercaptan and miscible with the alkyl chloride as well as with a minor proportion only of the hydrosulphide and water, said alcohol containing up to 10 per cent of its weight of water and the quantity of alcohol being less than that with which the water and hydrosulphide would be miscible; passing hydrogen sulphide into the mixture to saturate it therewith; incorporating the alkyl chloride with the mixture, the quantity of alkyl chloride being less than the molecular equivalent of the hydrosulphide and such that the water content of both phases of the mixture is not less than 7 per cent of the total weight; agitating the mixture at 85° to 110° C. and simultaneously passing hydrogen sulphide into it to maintain it saturated therewith; continuing the operation until the reaction is substantially complete with respect to the alkyl chloride; and recovering the product from the organic phase.

2. The process for production of alkyl mercaptans of 10 to 18 carbon atoms by reaction of the corresponding alkyl chloride with sodium hydrosulphide in a two-phase system which comprises agitating the hydrosulphide at 70° to 110° C. with water amounting to not less than substantially 43 per cent of the weight thereof, and an alcohol boiling above 85° but below the boiling point of the mercaptan and miscible with the alkyl chloride as well as with a minor proportion only of the hydrosulphide and water, said alcohol containing up to 10 per cent of its weight of water and the quantity of alcohol being less than that with which the water and hydrosulphide would be miscible; passing hydrogen sulphide into the mixture to saturate it therewith; incorporating the alkyl chloride with the mixture, the quantity of alkyl chloride being less than the molecular equivalent of the hydrosulphide and such that the water content of both phases of the mixture is not less than 7 nor more than 15 per cent of the total weight; agitating the mixture at 85° to 110° C. and simultaneously passing hydrogen sulphide into it to maintain it saturated therewith; continuing the operation until the reaction is substantially complete with respect to the alkyl chloride; and recovering the product from the organic phase.

3. The process for production of alkyl mercaptans of 10 to 18 carbon atoms by reaction of the corresponding alkyl chloride with crystalline sodium hydrosulphide in a two-phase system which comprises agitating the hydrosulphide at 70° to 110° C. with an alcohol boiling above 85° C., but below the boiling point of the mercaptan and miscible with the alkyl chloride as well as with a minor proportion only of hydrosulphide and its water of crystallization, said alcohol containing up to 10 per cent of its weight of water and the quantity of alcohol being less than that with which the water and hydrosulphide would be miscible; passing hydrogen sulphide into the mixture to saturate it therewith; incorporating the alkyl chloride with the mixture, the quantity of alkyl chloride being less than the molecular equivalent of the hydrosulphide and such that the water content of both phases of the mixture is not less than 7 per cent of the total weight; agitating the mixture at 85° to 110° C. and simultaneously passing hydrogen sulphide into it to maintain it saturated therewith; continuing the operation until the reaction is substantially complete with respect to the alkyl chloride; and recovering the product from the organic phase.

4. The process for production of alkyl mercaptans of 10 to 18 carbon atoms by reaction of the corresponding alkyl chloride with sodium hydrosulphide in a two-phase system which comprises agitating the hydrosulphide at 70° to 110° C. with water amounting to not less than substantially 43 per cent of the weight thereof, and an alcohol boiling above 85° C. but below the boiling point of the mercaptan and miscible with the alkyl chloride as well as with a minor proportion only of the hydrosulphide and water, said alcohol containing up to 10 per cent of its weight of water and the quantity of alcohol being less than that with which the water and hydrosulphide would be miscible; passing hydrogen sulphide into the mixture to saturate it therewith; incorporating the alkyl chloride with the mixture, the quantity of alkyl chloride being less than the molecular equivalent of the hydrosulphide and such that the water content of both phases of the mixture is not less than 7 per cent of the total weight; agitating the mixture at 85° to 110° C. and simultaneously passing hydrogen sulphide into the mixture to maintain it saturated therewith; continuing the operation until the reaction is substantially complete with respect to the alkyl chloride; washing the organic phase; drawing off the aqueous phase; and recovering the product from the organic phase.

5. The process for production of alkyl mercaptans of 10 to 18 carbon atoms by reaction of the corresponding alkyl chloride with sodium hydrosulphide in a two-phase system which comprises agitating the hydrosulphide at 70° to 110° C. with water amounting to not less than substantially 43 per cent of the weight thereof, and an alcohol of the group consisting of normal butyl, isobutyl, active amyl and beta butoxy ethyl alcohols, said alcohol containing up to 10 per cent of its weight of water and the quantity of alcohol being less than that with which the hydrosulphide and water would be miscible; passing hydrogen sulphide into the mixture to saturate it therewith; incorporating the alkyl chloride with the mixture, the quantity of alkyl chloride being less than the molecular equivalent of the hydrosulphide and such that the water content of both phases of the mixture is not less than 7 per cent of the total weight; agitating the mixture at 85° to 110° C. and simultaneously passing hydrogen sulphide into it to maintain it saturated therewith; continuing the operation until the reaction is substantially complete with respect to the alkyl chloride; washing the organic phase; drawing off the aqueous phase; and recovering the product from the organic phase.

6. The process for production of alkyl mercaptans of 10 to 18 carbon atoms by reaction of the corresponding alkyl chloride with sodium hydrosulphide in a two-phase system which comprises agitating the hydrosulphide at 70° to 110° C. with water amounting to not less than substantially 43 per cent of the weight thereof, and normal butyl alcohol containing up to 10 per cent of its weight of water, the quantity of alcohol being less than that with which the hydrosulphide and water would be miscible; passing hydrogen sulphide into the mixture to saturate it therewith; incorporating the alkyl chloride with the mixture, the quantity of alkyl chloride being less than the molecular equivalent of the hydrosulphide and such that the water content of both phases of the mixture is not less than 7 per cent of the total weight; agitating the mixture at 85° to 110° C. and simultaneously passing hydrogen sulphide into it to maintain it saturated therewith; con-

tinuing the operation until the reaction is substantially complete with respect to the alkyl chloride; washing the organic phase; drawing off the aqueous phase; and recovering the product from the organic phase.

7. The process for production of alkyl mercaptans of 10 to 18 carbon atoms by reaction of the corresponding alkyl chloride with sodium hydrosulphide in a two-phase system, which comprises agitating the hydrosulphide at 70° to 110° C. with water amounting to not less than substantially 43 per cent of the weight thereof, and isobutyl alcohol containing up to 10 per cent of its weight of water, the quantity of alcohol being less than that with which the hydrosulphide and water would be miscible; passing hydrogen sulphide into the mixture to saturate it therewith; incorporating the alkyl chloride with the mixture, the quantity of alkyl chloride being less than the molecular equivalent of the hydrosulphide and such that the water content of both phases of the mixture is not less than 7 per cent of the total weight; agitating the mixture at 85° to 110° C. and simultaneously passing hydrogen sulphide into it to maintain it saturated therewith; continuing the operation until the reaction is substantially complete with respect to the alkyl chloride; washing the organic phase; drawing off the aqueous phase, and recovering the product from the organic phase.

8. The process for production of alkyl mercaptans of 10 to 18 carbon atoms by reaction of the corresponding alkyl chloride with sodium hydrosulphide in a two-phase system which comprises agitating the hydrosulphide at 70° to 110° C. with water amounting to not less than substantially 43 per cent of the weight thereof, and active amyl alcohol containing up to 10 per cent of its weight of water, the quantity of alcohol being less than that with which the hydrosulphide and water would be miscible; passing hydrogen sulphide into the mixture to saturate it therewith; incorporating the alkyl chloride with the mixture, the quantity of alkyl chloride being less than the molecular equivalent of the hydrosulphide and such that the water content of both phases of the mixture is not less than 7 per cent of the total weight; agitating the mixture at 85° to 110° C. and simultaneously passing hydrogen sulphide into it to maintain it saturated therewith; continuing the operation until the reaction is substantially complete with respect to the alkyl chloride; washing the organic phase; drawing off the aqueous phase; and recovering the product from the organic phase.

9. The process for production of alkyl mercaptans of 10 to 18 carbon atoms free from colloidal impurities, by reaction of the corresponding alkyl chloride with sodium hydrosulphide in a two-phase system which comprises agitating the hydrosulphide at 70° to 110° C. with water amounting to not less than substantially 43 per cent by weight and an alcohol boiling above 85° C. but below the boiling point of the mercaptan and miscible with the alkyl chloride as well as with a minor proportion only of the hydrosulphide and water, said alcohol containing up to 10 per cent of its weight of water and the quantity of alcohol being less than that with which the water and

hydrosulphide would be miscible; passing hydrogen sulphide into the mixture to saturate it therewith; incorporating the alkyl chloride with the mixture, the quantity of alkyl chloride being less than the molecular equivalent of the hydrosulphide and such that the water content of both phases of the mixture is not less than 7 per cent of the total weight; agitating the mixture at 85° to 110° C. and simultaneously passing hydrogen sulphide into it to maintain it saturated therewith; continuing the operation until the reaction is substantially complete with respect to the alkyl chloride; washing the organic phase; drawing off the aqueous phase; washing the organic phase again with an electrolyte inert to the product; drawing off the aqueous phase again; and recovering the product from the organic phase.

10. The process for production of alkyl mercaptans of 10 to 18 carbon atoms free from colloidal impurities by reaction of the corresponding alkyl chloride with sodium hydrosulphide in a two-phase system which comprises agitating the hydrosulphide at 70° to 110° C. with water amounting to not less than substantially 43 per cent of the weight thereof, and an alcohol boiling above 85° C. but below the boiling point of the mercaptan and miscible with the alkyl chloride as well as with a minor proportion only of the hydrosulphide and water; said alcohol containing up to 10 per cent of its weight of water and the quantity of alcohol being less than that with which the water and hydrosulphide would be miscible; passing hydrogen sulphide into the mixture to saturate it therewith; incorporating the alkyl chloride with the mixture, the quantity of alkyl chloride being less than the molecular equivalent of the hydrosulphide and such that the water content of both phases of the mixture is not less than 7 per cent of the total weight; agitating the mixture at 85° to 110° C. and simultaneously passing hydrogen sulphide into it to maintain it saturated therewith; continuing the operation until the reaction is substantially complete with respect to the alkyl chloride; washing the organic phase; drawing off the aqueous phase; washing the organic phase again with strong brine solution; drawing off the aqueous phase again; and recovering the product from the organic phase.

11. The process for production of Lorol mercaptan which comprises agitating crystalline sodium hydrosulphide at 70° to 110° C. with normal butanol containing up to 10 per cent water in the proportions of substantially 970 to 1,500 parts by weight; passing hydrogen sulphide into the mixture to saturate both phases therewith; incorporating Lorol chloride in the proportion of substantially 1,700 parts by weight with the mixture; agitating the mixture at 85° to 110° C. and simultaneously passing in hydrogen sulphide to maintain it saturated therewith; continuing the operation until the reaction is complete with respect to the Lorol chloride; washing the organic phase; drawing off the aqueous phase; washing the organic phase again with a strong brine solution; drawing off the aqueous phase again; and recovering the product from the organic phase.

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