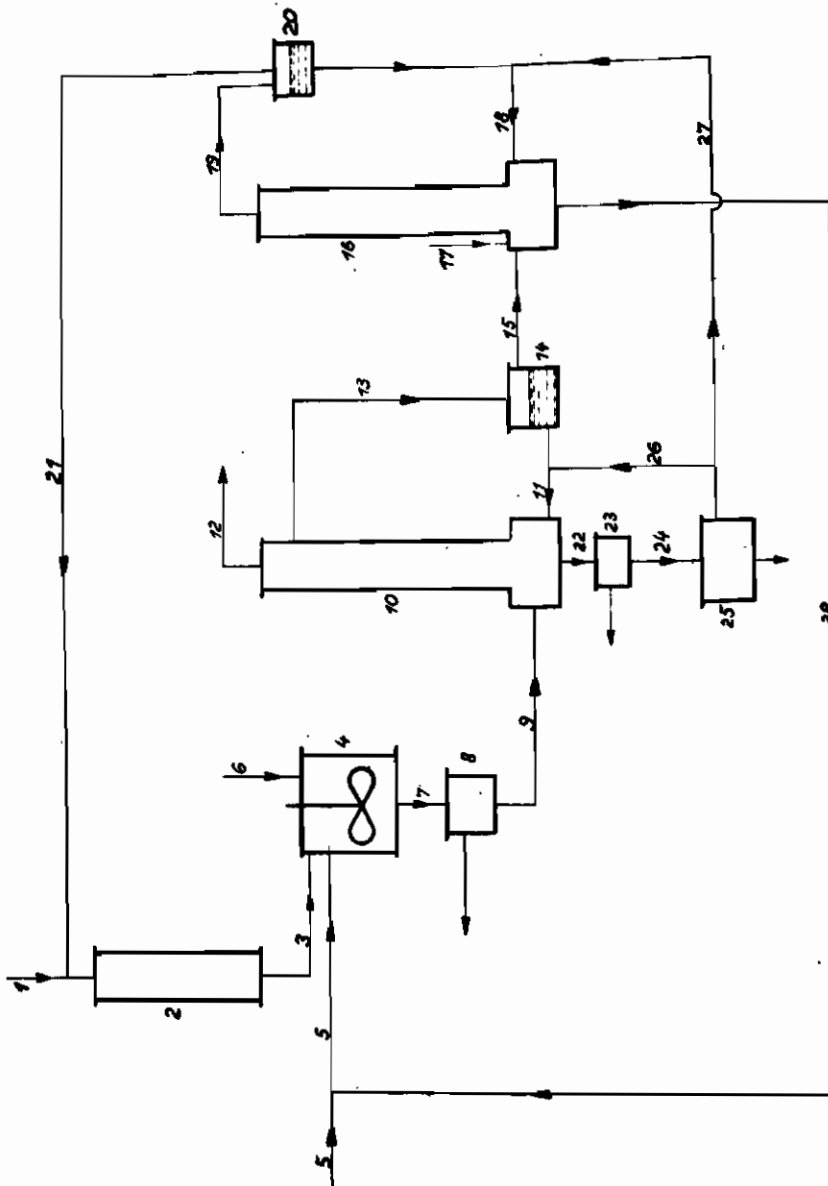


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PROCESS FOR THE PRODUCTION OF OXIMES
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ALIEN PROPERTY CUSTODIAN

PROCESS FOR THE PRODUCTION OF OXIMES

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The present invention relates to a process for the production of oximes.

I have found that the oximes of cyclohexanones (including cyclohexanone itself, its homologues and mixtures thereof) can be prepared in an advantageous manner by starting, instead of from pure cyclohexanones, from their mixtures with cyclohexanols, such as are obtained in the production of cyclohexanones by catalytic dehydrogenation of cyclohexanols. According to my invention the cyclohexanones are converted into oximes while in admixture with the cyclohexanols and the major portion of the oximes which separates out in a solid state is removed, for example by filtration or centrifuging, whereupon the residual liquid is subjected to a rectifying distillation with steam. This distillation yields first runnings of any cyclohexenes if such are present at all; then, contrary to expectation, the total amount of the cyclohexanols containing but slight proportions of oximes distills over; the proportion of oximes contained in the cyclohexanols, varies depending on the distillation conditions between about 1 and 6 per cent only of the total quantity of oximes. These cyclohexanol-cyclohexanone oxime mixtures obtained by the distillation with steam are preferably worked up by reconvertng the oximes into cyclohexanones by treatment with an excess of acid, distilling the mixture of cyclohexanols and cyclohexanones obtained (advantageously by means of steam) and subjecting it to dehydrogenation in order to convert the cyclohexanols into cyclohexanones, which then are again converted into oximes and so on.

The distillate obtained by subjecting such mixtures of oximes and cyclohexanols subsequently to their treatment with an acid to a distillation with steam (as described above) contains, in addition to the cyclohexanols, only about half the calculated amount of cyclohexanones. A solution of oximes and hydroxylamine salts remains behind as the residue of this steam distillation, from which the oximes may be set free by the addition of alkali. The said solution of the salt containing oxime and hydroxylamine can also be added directly to a fresh portion of the initial mixture of cyclohexanones and cyclohexanols to be converted into oximes and so directly returned to the process. It is advantageous that the treatment with an excess of acid yields a larger proportion of oxime salt, because this can be directly returned to the stage in which the oxime is formed. In this manner, all

of the substances employed for the reaction are completely utilized.

The use of crude cyclohexanones containing cyclohexanols offers considerable advantages. Cyclohexanones, as is known, are prepared by the catalytic dehydrogenation of cyclohexanols in the vapor phase, in which treatment part of the cyclohexanols, usually from about 10 to 20 per cent, remains unchanged. The separation of these unchanged cyclohexanols, however, is difficult and expensive to perform, since the cyclohexanones, which are by far preponderant in quantity to the cyclohexanols, must be distilled off from the latter. With mixtures of homologues the separation of the single components and also a sharp separation of the total quantity of the cyclohexanols from the cyclohexanones, is altogether impossible or hardly possible for the reason that the boiling points of the components of such mixtures overlap, as appears from the following table:

Substance	Boiling point
	°C
Cyclohexanone.....	155
2-methylcyclohexanone.....	165
3-methylcyclohexanone.....	169
4-methylcyclohexanone.....	171
Dimethylcyclohexanones.....	170-182
Cyclohexanol.....	160
2-methylcyclohexanols.....	166-169
3-methylcyclohexanols.....	171-174
4-methylcyclohexanols.....	173-175
Dimethylcyclohexanols.....	179-189

From such mixtures cyclohexanone can be distilled off in a purity of about 98 per cent only. If such product is used for the conversion into oxime by the usual method a loss of cyclohexanol occurs. The process in accordance with the present invention, in contrast thereto, allows to produce pure oximes without the occurrence of losses in cyclohexanones or cyclohexanols. It is surprising that the cyclohexanols can be separated smoothly and with no danger whatever from the oximation mixture by steam distillation, since the ordinary distillation of a mixture of cyclohexanoneoximes and cyclohexanols presents the serious danger of a decomposition and explosion, even when being carried out under reduced pressure. Moreover, it was to be expected that the cyclohexanoneoximes would be reconverted by steam into the cyclohexanones. As a matter of fact such a reversion does not occur.

The following Example will further illustrate with reference to the accompanying diagram-

matic drawing how the invention may be carried out in practice but the invention is not restricted to this Example.

Example

Cyclohexanol is delivered through line 1 to a vessel 2 in which it is dehydrogenated in known manner with the aid of catalysts at an elevated temperature. The product so obtained which consists, for example, of 84.5 per cent of cyclohexanone, 15 per cent of cyclohexanol and 0.5 per cent of cyclohexene, is passed through line 3 into the stirring vessel 4; a mixture of the calculated quantity of hydroxylamine sulphate with twice its quantity of water is supplied to the said vessel 4 through line 5. The reaction mixture is vigorously stirred and cooled, while introducing through line 6 sufficient gaseous ammonia to neutralize the sulphuric acid liberated during the reaction.

The reaction mixture is conveyed through line 7 to the centrifuge 8 where pure cyclohexanone oxime is separated in an amount of about 87 per cent (with reference to cyclohexanone contained in the mixture employed). The liquid freed from solid oxime consists of an aqueous solution of ammonium sulphate and a solution of cyclohexanone oxime which has not separated out and cyclohexene in cyclohexanol; it is passed through line 9 into a still provided with the distilling column 10 where it is subjected to a rectifying distillation with steam generated from water supplied through line 11. During this distillation an azeotropic mixture of a little water and the cyclohexene is taken out at the top of the column through line 12 at a temperature of about 70°C. Through line 13 a mixture of about 80 per cent of cyclohexanol and about 20 per cent of cyclohexanone oxime together with steam distills into the separator 14 where the water

separates as a layer; it is conveyed through line 15 to the still of the distilling column 16. The upper layer passes through line 17 into the still of the distilling column 18. Through line 19 an excess of sulphuric acid of 10 per cent strength is introduced; water is supplied through line 20 and evaporated in the still of column 18. The distillate from this steam-distillation flows through line 21 into the separator 22 where the water separates as a bottom layer from the mixture consisting of about 90 per cent of cyclohexanol and about 10 per cent of cyclohexanone. The water is returned to the still of column 18 through line 23 and the mixture of cyclohexanol and cyclohexanone passed back to the dehydrogenation vessel 2 through line 24.

The residue remaining in the still of the distilling column 16, consisting of cyclohexanone oxime and an aqueous solution of ammonium sulphate, passes through line 25 into the centrifuge 26 where the oxime is separated off. Its amount corresponds to about 10 per cent of the cyclohexanone employed. The solution of ammonium sulphate is led off through line 27 to the vessel 28 where it is evaporated to dryness. The sulphate may be used for fertilizing purposes. The steam generated during the evaporation may be passed to the stills of the distilling columns 10 and 16 through lines 29 or 30 and 31, respectively, if so desired.

The distillation residue remaining in the still of column 18 consists of an aqueous solution of cyclohexanone oxime sulphate and hydroxylamine sulphate. This mixture is led back through lines 32 and 33 to the stirring vessel 4 or the oxime is set free by means of alkali and recovered by filtration or centrifuging.

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