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3,523,967

## PROCESS OF PURIFICATION

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8 Claims

## ABSTRACT OF THE DISCLOSURE

A process of removing quaternary ammonium compounds from aliphatic dinitriles, dicarboxylates and tetracarboxylates in an aqueous system, by dissolving the nitriles etc. in a solvent, cooling the resultant solution below 0° C. until the bulk of the quaternary ammonium compound precipitates and separating it, together with any ice formed. The quaternary ammonium compound may also be absorbed on to a solid phase and separated from the cooled solution.

This invention relates to a process of recovery of useful chemical substances; in particular it relates to a process of recovery of quaternary ammonium compounds from the reaction mixture of the hydrodimerization process of olefinic nitriles.

In our co-pending U.S. application Ser. No. 446,430, filed Apr. 7, 1965 we describe a process for the hydrodimerization of olefinic nitriles, in particular of acrylonitrile in aqueous solutions of quaternary ammonium compounds, using alkali amalgams as reducing agents. When acrylonitrile is used as the starting material the product from this process is adiponitrile; the latter, whether now separating from the aqueous phase spontaneously or extracted with a solvent, usually carries with it a proportion of the quaternary ammonium compound used. It is desirable for economic reasons to recover and recycle as much of this as possible. Water-extraction from the adiponitrile (or its solution in a solvent) would appear to be an obvious means of recovery. We have, however, found that with certain types of quaternary ammonium compounds, particularly with those having one or more long alkyl groups in the molecule, the water extraction is difficult to take to completion, since the partition coefficient of the quaternary compound becomes progressively more unfavorable as its concentration in the adiponitrile (or the adiponitrile solution) falls. A large volume of water is required for reasonable recovery even if efficient countercurrent extraction apparatus is used. This is impractical since the quaternary compound is to be returned to the main process and excessive amounts of water and build-up of the aqueous reactant volume must be avoided. Complete recovery of quaternary by water extraction has, in fact, proved to be virtually impossible in some cases, for example with cetyl trimethyl ammonium bromide.

We have now found that it is possible, without water extraction, to recover most of the quaternary compound in one step and to recover virtually all the remainder of the quaternary compound in a subsequent step; this effects a substantial simplification of the process. Furthermore our process permits removal of the water already mixed with the adiponitrile and derived from the hydrodimerization reagent mixture. This simplifies the separation of the unreacted acrylonitrile, which is present in the adiponitrile, from the undesired by-product propionitrile, since the formation of water azeotropes interfering with the sep-

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aration step of acrylonitrile from propionitrile by distillation is avoided.

Accordingly we provide a process of removing quaternary ammonium compounds from aliphatic dinitriles formed by reductive hydrodimerization of olefinic nitriles in the presence of quaternary ammonium compounds which process comprises dissolving said dinitrile in a solvent such that the freezing or crystallization point—whichever is the higher—of the resultant solution is below 0° C., cooling said solution to a temperature below 0° C., but above the freezing or crystallization point—whichever is the higher—of said solution of the dinitrile, until the bulk of the quaternary ammonium compound precipitates, and separating by means known per se the said precipitate together with other solids, particularly the ice formed.

The quaternary compound thus recovered may then be recycled to the process of our copending application.

The present process is applicable to the recovery of quaternary ammonium compounds from the reaction products of the hydrodimerization of acrylonitrile and alkyl substituted acrylonitriles to the corresponding dinitriles, particularly from the hydrodimerization of acrylonitrile to adiponitrile.

By the term "alkyl substituted acrylonitriles" throughout this specification we mean acrylonitrile bearing at least one alkyl substituent having up to 4 carbon atoms attached to the alpha or beta carbon atoms joined by the double bond. However, it is already known from Australian Pat. 263,328 that in respect of hydrodimerization the alpha, beta mono-olefinic mono- or di-carboxylates as defined in the Australian patent are equivalent to the corresponding nitriles. Hence it is within our invention to apply the process as described in an analogous manner to the hydrodimerization of mono- or dicarboxylates to paraffinic di- or tetra-carboxylates.

The quaternary compounds to which our process is particularly applicable are described in Ser. No. 446,430; among these it is especially useful for the quaternary compounds having one or two alkyl substituents longer than decyl.

Solvents suitable for our process are characterized in that they are good solvents for the dinitrile, i.e. 100 g. of the solvent should dissolve at least 100 g. of the dinitrile at room temperature, and that they are poor solvents as defined below for the quaternary compound.

For a given reaction product from the hydrodimerization process containing  $x$  grams of the dinitrile and  $y$  grams of the quaternary compound it should, theoretically, suffice to treat the product as described with a solvent having a solubility ratio of the dinitrile and the quaternary compound  $x/y$ . However, as long as the solubility ratio is only a few times larger than  $>x/y$ , say

$$5 \frac{x}{y} \text{ or } 10 \frac{x}{y}$$

the reduction in quaternary compound content is only marginal; the reason for this is the co-solvent effect of the dinitrile on the quaternary compound. For economic reasons it is desirable that the dinitrile concentration in the solvent is high. Consequently we prefer that the dinitrile is highly soluble, most preferably miscible with the solvent and that the quaternary compound is soluble in the solvent to the extent of less than 3%, preferably less than 0.1% and most preferably less than 0.01%, all by weight. It is, of course, possible to reduce the co-solvent effect of the dinitrile and to operate our process with less desirable solvents by increasing the proportion of solvent to the dinitrile, and such operation is within the limits of this invention; however, since recovery of solvent by

distillation and solvent losses are expensive, this is obviously less preferred.

Suitable solvents are e.g.:

Class	Solubility of adiponitrile at 20° C.	Solubility of cetyl trimethyl ammonium bromide, g./100 mls. solvent, 20° C.	Solubility of cetyl trimethyl ammonium bromide in mixture of 2 parts solvent 1 part adiponitrile g./100 mls. Temp. (°C)	
Class 1:				
Methylene chloride.....	Miscible.....	3.5	1.6	-36
Acetone.....	do.....	0.13	1.1	-25
Ethyl acetate.....	do.....	0.014	2.6	-20
Class 2:				
Trichloroethylene.....	do.....	0.0073	0.83	-17
Monochlorobenzene.....	do.....	0.0022	0.70	-20
Class 3:				
Xylene.....	do.....	0.0058	0.43	-15
Ethylbenzene.....	do.....	0.0026	0.30	-25
Toluene.....	do.....	0.0017	0.23	-25

It is apparent that Class 2 solvents are preferred and Class 3 solvents are most preferred.

The weight ratio of solvent to dinitrile is not narrowly critical; it may vary over a wide range e.g. from 1:5 to 5:1 and greater than 5:1; too little solvent causes too small a depression of the freeing point; large amounts of solvent, while usually effective up to very high ratios, are uneconomical.

Thus we have found that when a solution of pure adiponitrile in toluene, saturated with cetyl trimethyl ammonium bromide (referred to hereinafter as CTAB) was cooled, the residual CTAB remaining in solution at the point of crystallization of adiponitrile, was as follows:

Ratio v/v toluene/adiponitrile	CTAB expressed as w/v percent of adiponitrile	Crystallization point of adiponitrile (° C.)
1/1.....	1.5	-10
2/2.....	0.8	-17
3/1.....	0.5	-18
4/1.....	0.375	-18

Beyond 4/1 parts v/v of toluene the improvement is small, and it appears that a little cetyl trimethyl ammonium bromide would still remain in solution even at very high dilution.

Methods of separating the precipitate of quaternary ammonium compound, optionally together with ice and other impurities are known; decantation, filtration or centrifuging are optional alternatives.

We also provide a further process comprising treating a solution of a dinitrile in a solvent containing also a small amount of quaternary ammonium compound, e.g. the organic solution resulting from the above described crystallization step after separation of the bulk of the quaternary compound, with an adsorbant for quaternary ammonium compounds; separating the adsorbent together with the adsorbed quaternary compound from said solution; optionally, extracting the quaternary compound from said adsorbent and recovering both adsorbent and the quaternary compound.

This process of adsorption preferably is carried out in conjunction with the preceding crystallization step. When the concentration of quaternary compound in the dinitrile is low it is, however, possible to omit the crystallization step; in that case it may suffice to add only a small amount of a solvent for said dinitrile to the dinitrile, so as to reduce its viscosity or, alternatively, the liquid dinitrile may be used by itself and the quaternary agent is removed from it by adsorption.

Accordingly we also provide a process of treating a dinitrile containing small amounts of a quaternary agent with an adsorbent for said quaternary agent and removing the latter thereby from the dinitrile.

The solvent in this case may be any comparatively non-

polar liquid which is miscible with dinitrile e.g. acrylonitrile, chlorinated hydrocarbons, benzene, toluene, etc.

The water content of the dinitrile should be kept as low as possible since water reduces the capacity of the adsorbent for the quaternary compound.

Suitable adsorbents are finely divided polar solid substances which are chemically inert to the dinitrile and the solvent and are capable of adsorbing at least 2%, preferably at least 20% of their weight of the quaternary compound such as e.g. silica gel, active alumina and siliceous and aluminous substances e.g. clay, fuller's earth. Other suitable adsorbents may be selected by determination of their adsorptivity in respect of quaternary ammonium compounds. Means of separating the adsorbent are known per se, decantation filtration and centrifuging are suitable. The adsorbent may be used in column form.

The temperature at which the adsorption process is carried out is not narrowly critical; a suitable range is from, say, -10° C. to ambient or higher temperature.

The adsorbent may be recovered after the quaternary compound has been dissolved off e.g. by drying at elevated temperatures.

Recovery of the adsorbed quaternary from the solid adsorbent is advantageously performed with a volatile, highly polar liquid such as methanol.

Yet a further process according to this invention comprises recovering the dinitrile from the filtrate solution after the processes of removal of the quaternary compound as heretofore described by further cooling the solution and crystallizing out the dinitrile. Alternatively the solvent and the low boiling other components, in the case of hydrodimerization of acrylonitrile, principally acrylonitrile and propionitrile, are removed by distillation; however crystallization of the dinitrile is preferred since the evaporation of large amounts of solvent is expensive. A further variant of our recovery process of dinitrile by crystallization of the dinitrile from the solvent comprises removing the crystallized dinitrile and distilling only sufficient of the remaining solute to strip off residual low boiling impurities, particularly the acrylonitrile or substituted acrylonitrile respectively and the corresponding saturated nitrile e.g. propionitrile and recycling the remaining solute containing dinitrile to the next reaction cycle.

Our invention is now illustrated by but not limited to the following examples.

#### EXAMPLE 1

100 ml. of a reaction product from the hydrodimerization process containing 50.2% adiponitrile 30% acrylonitrile, 7.8% CTAB, 1% propionitrile, water and a trace of sodium bicarbonate was mixed with twice its volume of toluene. The mixture was cooled to -25° C., held at this temperature for 15 minutes, and was then filtered. The filtrate contained 0.14% by weight of CTAB.

#### EXAMPLE 2

A solution in toluene of dinitrile obtained from the hydrodimerization process and treated as described in Example 1 contained 0.835 g. CTAB for every 100 g. adiponitrile in solution.

A glass tube of 2 cm. internal diameter, and fitted near one end with a sintered glass disc was packed partially with 13 grams of crushed silica gel ( $\approx$ 100 mesh).

At a temperature of 20° C. the solution was forced through the silica gel bed under pressure at a flow-rate of 25 ml./minute. The effluent was periodically analysed for CTAB. The first 900 ml. of effluent contained approximately 0.0035 g. CTAB per 100 g. of adiponitrile in solution. At this stage the silica gel had taken up 15 g. of CTAB per 100 g. adsorbent. After 1300 ml. had been eluted the concentration of CTAB had risen to 0.020 g./100 g. adiponitrile in solution; take-up of CTAB at this stage was 22 g. CTAB/100 g. silica gel. Beyond this point, the concentration of CTAB in the effluent rose rapidly,

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reaching 0.8 g. CTAB/100 g. adiponitrile in solution at 1500 ml. eluted; CTAB take-up of 24 g./100 g. silica gel.

## EXAMPLE 3

A solution of hydrodimerization product in toluene as used in Example 2 was run through a column packed with crushed alumina (80 mesh) kept at 20° C. The effluent contained 0.008 g. CTAB/100 g. adiponitrile in solution until the adsorbent had taken up 6 g. CTAB/100 g. alumina, at which point the CTAB concentration started to rise rapidly until it reached 0.8 g./100 g. adiponitrile in solution when 7 g. of CTAB/100 g. alumina had been taken up.

## EXAMPLE 4

Portions of the solution used in Example 2 were shaken up with differing amounts of fuller's earth at 20° C. After shaking up for a few minutes, the solutions were filtered and analysed for CTAB. The following table shows the weight of CTAB taken up and the weight remaining in solution.

Run	G. CTAB taken up per 100 g. fuller's earth used	G. CTAB/100 g. adiponitrile in filtered solution
1.....	2	0.004
2.....	5	0.009
3.....	8	0.019
4.....	12	0.043
5.....	16	0.104
6.....	19	0.30
7.....	22	0.65

## EXAMPLE 5

The column packed with 13 g. silica gel used in Example 2 was blown through with compressed air to remove most of the residual toluene solution. At this stage the silica gel was calculated to have adsorbed 3.11 g. CTAB. 70 ml. of methanol was passed through this column at 20° C. Analysis of the methanol showed that it contained 2.80 g. CTAB—i.e. a 90% recovery of CTAB was obtained.

## EXAMPLE 6

A glass tube 1.5 cm. internal diameter was packed with 10 g. silica gel to give an 11 cm. long bed. Adiponitrile containing 1.09 g. CTAB per 100 g. adiponitrile was passed through the column at the rate of 6 ml. per hour. The temperature of the adsorbent was 22° C. The effluent from the column was periodically analysed for CTAB.

Grams CTAB adsorbed per 100 g. silica gel:	Grams CTAB in effluent per 100 g. adiponitrile
0.99 .....	<0.01
2.24 .....	<0.01
5.28 .....	<0.01
7.46 .....	0.017
9.42 .....	0.018
12.1 .....	0.017
13.8 .....	0.083
15.2 .....	0.10
16.4 .....	0.22
18.0 .....	0.32
18.7 .....	0.80

## EXAMPLE 7

3.8 g. silica gel was packed into a tube of 8 cm. internal diameter to give 1 cm. bed height. Adiponitrile, containing 4.17 g. CTAB per 100 ml. adiponitrile, was passed through the bed. The column was kept at 60° C. The effluent from the column was periodically analysed for CTAB.

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Grams CTAB adsorbed per 100 g. silica gel:

Grams CTAB in effluent per 100 g. adiponitrile

4.61 .....	<0.01
7.81 .....	<0.01
9.34 .....	<0.01
10.8 .....	<0.01
18.4 .....	<0.01
26.9 .....	<0.01
29.5 .....	<0.01
32.8 .....	0.017
37.8 .....	0.87
38.4 .....	2.75
39.8 .....	3.52

## EXAMPLE 8

A run similar to that described in Example 7 was carried out using however the organic phase directly as obtained from the hydrodimerisation of acrylonitrile to adiponitrile; its composition was that of the starting material of Example 1. The following results were obtained.

Grams CTAB adsorbed per 100 g. silica gel:

Grams CTAB per 100 g. adiponitrile in effluent

2.3 .....	<0.01
7.0 .....	<0.01
9.0 .....	1.65
9.05 .....	5.03

We claim:

1. In the process of removing quaternary ammonium compounds from adiponitrile or alkyl-adiponitrile formed by the reductive hydrodimerization of a nitrile starting material selected from acrylonitrile or alkyl-acrylonitrile, respectively, wherein a liquid dimerization medium containing the starting material is brought into contact with an alkali metal or alkaline earth metal amalgam, there being included in said liquid medium at least one water soluble ionizable alkylated quaternary ammonium salt and maintaining said liquid medium at a pH of at least 1.5 and a temperature less than 60° C., the improvement which comprises mixing the reductive dimerization medium containing said adiponitrile or alkyl-adiponitrile with an inert organic solvent which gives a solution containing at least 100 grams of the nitrile product per 100 grams of the solvent at room temperature and less than 3 grams of the quaternary salt at said temperature, said solution having a freezing or crystallization point, whichever is the higher, of below 0° C., cooling the resulting solution to a temperature below 0° C. but above the freezing or crystallization point, whichever is the higher, of said solution whereby the quaternary ammonium compound contained in the solution is precipitated, and separating the said precipitate.

2. A process according to claim 1 wherein the starting material is acrylonitrile and the product adiponitrile is miscible in the solvent.

3. A process according to claim 1 wherein 100 g. of the solvent at room temperature is capable of dissolving at least 100 g. of adiponitrile and the quaternary ammonium compound is soluble in the solvent to the extent of less than 0.1% w./w.

4. A process according to claim 1 wherein the solvent is selected from the group consisting of methylene dichloride, acetone, ethyl acetate, trichloroethylene, monochlorobenzene, xylene, ethylbenzene and toluene.

5. A process according to claim 2 wherein the solvent is a hydrocarbon solvent and the ratio by weight of hydrocarbon solvent to adiponitrile is from 1:5 to 5:1 and wherein after separating the solid crystallized quaternary ammonium compound, the mother liquor resultant from said separation and containing a residual amount of quaternary ammonium compound is treated with an adsorbent, said adsorbent being a finely divided polar solid substance which is chemically inert to said adiponi-

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trile and the solvent and which is capable of adsorbing at least 2% of its weight of said quaternary ammonium compound; and separating the adsorbent together with the adsorbed residual amount of quaternary ammonium compound from said mother liquor.

6. A process according to claim 5 which comprises in addition recovering the adiponitrile in the mother liquor by further cooling the said mother liquor and crystallising out therefrom said adiponitrile.

7. A process according to claim 5 wherein the adsorbent is selected from the group consisting of silica gel, active alumina, siliceous earths and aluminous earths.

8. A process according to claim 1 wherein the solution remaining after precipitation and separation of said quaternary ammonium compound is treated with a finely

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divided polar solid adsorbent for any residual quaternary ammonium compound remaining in said solution and separating the adsorbent together with the residual quaternary ammonium compound adsorbed therein from the remaining solution.

#### References Cited

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JOSEPH P. BRUST, Primary Examiner

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