



SOLVENT TRANSFER PROCESS FOR DINITROGEN PENTOXIDE

This invention relates to a process for the recovery of dinitrogen pentoxide, N_2O_5 , from an anolyte loop of an electrochemical cell into an alternative solvent system.

It is known to produce N_2O_5 by an electrochemical process. Such a process is described in GB Patent No. 2 245 003 in the name of one of the co-applicants.

Overall, such a process involves the conversion of HNO_3 to N_2O_5 and water, with N_2O_4 playing a role in the electrochemical reactions. The product is N_2O_5 in solution in HNO_3 with a small amount of N_2O_4 impurity. The concentration of N_2O_5 in this product is typically around 32 wt.% which is close to the saturation point for this solute/solvent system.

The importance of N_2O_5 has recently increased due to its application in the synthesis of energetic compounds, and particularly energetic polymers such as poly(3-nitratomethyl-3-methyloxetane) (polyNIMMO) or Poly glycidyl nitrate (PolyGLYN).

For use in organic nitration processes it is desirable that the N_2O_5 should be available in an inert organic solvent, such as dichloromethane. This could be achieved by solvent extraction from an HNO_3 solution. However such a process would be prohibitively costly to construct and operate, requiring substantial fixed plant. There would also be a likelihood of back-contamination of any electrolytic circuit by the organic solvent through recycling of the HNO_3 .

It is known from USSR Inventor's Certificate SU-1089047A that solid N_2O_5 can be separated from strong 35-40 wt.% solutions of N_2O_5 in nitric acid by the addition of moderate amounts of N_2O_4 at a temperature of -5 to 0°C.



This results in precipitation of N_2O_5 contaminated with considerable amounts of HNO_3 from the solution. The presence of HNO_3 in this solid N_2O_5 makes it unsuitable for use in specific organic nitration procedures involving acid sensitive substrates. Relatively pure N_2O_5 can be obtained from this solid material by low pressure sublimation and subsequent condensation onto a cold surface. The overall procedure, however, then becomes lengthy and cumbersome and as such not suited to an industrial process. Moreover, this method of N_2O_5 production requires a starting solution of N_2O_5 in HNO_3 which is electrochemically less efficient and more costly to produce because of the very low proportion of N_2O_4 which it must contain.

In UK Patent No. 2 245 266 in the name of one of the co-applicants, there is disclosed a method of N_2O_5 separation, wherein a solution of N_2O_5 in HNO_3 at a temperature of at least $10^\circ C$ (and containing at least 45 weight percent of dissolved N_2O_4 and N_2O_5 and further having a dissolved N_2O_5 : HNO_3 ratio by weight of at least 1:3) is cooled to less than $8^\circ C$ until an N_2O_5 solvate precipitates from the solution. The disclosure teaches that formation of a separate liquid N_2O_4 phase is to be avoided since this reduces the yield of N_2O_5 solvate, with a proportion of the N_2O_5 instead entering the liquid N_2O_4 phase. This is particularly true for temperatures below about 0 to $-5^\circ C$, at which the N_2O_4 tends more readily to form a separate liquid phase.

It has been found that if the N_2O_5/HNO_3 mixture obtained from the electrochemical process for producing N_2O_5 is maintained at or near saturation with N_2O_4 and then cooled, phase separation takes place in which N_2O_4 is the principal solvent of one phase and HNO_3 the principal solvent of the other phase. N_2O_5 is present within, and in equilibrium between, the two phases. The two phases may be readily separated and the N_2O_5 in the N_2O_4 phase can

be efficiently extracted therefrom. The N_2O_5 extracted from the N_2O_4 phase can then be taken up into a suitable organic solvent either directly by extraction or by dissolution following isolation of solid N_2O_5 ". It has been found that N_2O_5 can be produced in an organic solvent in a more pure form than has previously been achieved through extraction from a (mainly) nitric acid solution as described above.

Further, it has been found that by using only a small proportion of the recirculating anolyte stream of the electrochemical process, N_2O_5 can be effectively stripped out of the mixture on a continuous basis without disrupting the steady state operation of the electrochemical process.

Accordingly, a first aspect of the present invention provides a process for producing a solution of N_2O_5 in an organic solvent, comprising the steps of:

passing anolyte and catholyte streams of N_2O_4 in HNO_3 through respective anode and cathode compartments of an electrochemical cell whilst applying a potential difference between an anode and a cathode thereof, whereby electrical current is passed through the cell and N_2O_5 is electrochemically formed in the anode compartment, characterised by the further steps of:

dividing off a portion of the anolyte stream and causing the divided portion to separate to produce a first N_2O_4 solvent phase containing N_2O_5 and a second HNO_3 solvent phase also containing N_2O_5 ;

separating the two phases in a separator; and

recovering N_2O_5 from the first N_2O_4 phase into an organic solvent, to produce a solution of N_2O_5 therein.





The electrolytic process should preferably be operated at a maximum possible temperature which is consistent with the need to avoid decomposition of the materials involved.

An exit temperature for the anolyte stream in the range of 0 - 30°C is preferable, more preferably in the range 15 - 25°C. By this means it may be sought to optimise the efficiency of the overall process of the invention since the higher the temperature of the starting solution, that is the anolyte stream, the greater can be the quantity of N_2O_5 and N_2O_4 dissolved and therefore the greater will be the quantity of N_2O_5 in the final separated N_2O_4 Phase and so available for crystallisation.

Preferably, the electrochemical process should operate with the anolyte stream close to saturation with respect to N_2O_4 , the concentration of N_2O_4 typically being at least 20 wt%, and preferably, at least 30 wt% of the anolyte stream.

The divided portion of the anolyte stream may be caused to separate into two phases either by cooling or by addition thereto of N_2O_4 such that the divided portion becomes over saturated with respect to N_2O_4 . Addition of further N_2O_4 in this way also has the advantage of increasing the volume of the separated N_2O_4 layer and hence the amount of N_2O_5 which may be removed from the system as product.

The added N_2O_4 may consist of fresh liquid N_2O_4 recovered/recycled N_2O_4 from a previous recovery processs, or a combination of both.

Alternatively, a combination of addition of N_2O_4 with cooling may be used to cause two liquid phases to form. In this case it is preferred to add N_2O_4 to the divided

portion of the anolyte stream before the portion passes to the separator in order to ensure that the portion is saturated with N_2O_4 . Prior to cooling.

According to a second aspect of the present invention therefore there is provided a process for producing a solution of N_2O_5 in an organic solvent comprising the steps of:

passing anolyte and catholyte streams of N_2O_4 in HNO_3 through respective anode and cathode compartments of an electrochemical cell whilst applying a potential difference between an anode and a cathode thereof, whereby electrical current is passed through the cell and N_2O_5 is electrochemically formed in the anode compartment, characterised by the further steps of:

dividing off a portion of the anolyte stream, saturating the divided portion with N_2O_4 by addition thereto of N_2O_4 with thorough mixing, to produce a first N_2O_4 solvent phase containing N_2O_5 and a second HNO_3 solvent phase also containing N_2O_5

separating the two phases in a separator; and

recovering N_2O_5 from the first N_2O_4 Phase into an organic solvent to produce a solution of N_2O_5 therein.

Preferably the process further comprises cooling the divided portion subsequent to its saturation with N_2O_4 .

It is worth noting that use of such essentially simple variables to control the process of the present invention emphasises the advantage of the present process over more elaborate counter-current type extraction processes.



Where two phases are produced simply by cooling the divided portion of the anolyte stream, because partitioning of the N_2O_5 is taking place from an homogeneous solution, the proportion of N_2O_5 in the two phases is instantaneously in the equilibrium proportion making the partition more efficient than that of simple solvent extraction where mass transfer considerations must be taken into account. Even where excess N_2O_4 is added to the divided portion of the anolyte stream (and either with or without subsequent cooling), such that the partition which occurs is not strictly under equilibrium conditions, in practice the results are essentially very similar, provided the addition takes place with efficient mixing. It is necessary that where the divided portion is to be cooled, it should have been thoroughly mixed beforehand.

Where the divided portion is cooled, this should be to a temperature of around -5 to $+15^\circ\text{C}$.

Further, the process should preferably operate with the anolyte stream close to saturation with respect to N_2O_5 compatible with the avoidance of crystallization of N_2O_5 in the anolyte stream. Typically, the concentration of N_2O_5 will be at least 15 wt% and preferably at least 20 wt%.

The electrochemical cell preferably employs a cationic exchange membrane (such as that described in UK Patent No. 2 245 003 in the name of one of the co-applicants), so that increases in the mass of HNO_3 in the anolyte stream by intra-cell transfer from the catholyte is avoided. Use of an anionic membrane would allow HNO_3 to pass through from catholyte to anolyte such as to effectively render continuous operation of the electrochemical and phase separation processes uneconomic.



Preferably the divided portion of the anolyte stream is a minor portion thereof. This allows the cell and process to be operated continuously. The portion of the anolyte stream divided off is advantageously such that, under the conditions of transfer of N_2O_5 which exist downstream, the amount of transferred N_2O_5 will substantially equal the amount of N_2O_5 being generated in the cell. In this way the cell, and hence the process, may be operated in a steady state manner.

Preferably the divided portion is approximately 1 wt% to 20 wt% of the anolyte stream, and more preferably approximately 5 wt% thereof.

Recovery of N_2O_5 from the N_2O_4 Phase may be accomplished in a number of ways, for example, abstraction (extraction) or distillation (evaporation). Possible recovery methods include:

chilling the N_2O_4 phase to induce crystallization either in bulk or on a cold surface and then respectively filtering off the solid or draining the liquid phase from the surface, followed by re-dissolving the solid N_2O_5 in an organic solvent; or

applying reduced pressure to the N_2O_4 phase to cause the solvent N_2O_4 to be distilled off and re-dissolving the N_2O_5 produced in an organic solvent; or

feeding the N_2O_4 phase directly into an organic solvent and subjecting the mixture to fractional distillation at reduced pressure to remove the volatile N_2O_4 , leaving a solution of N_2O_5 in the organic solvent.

Any residual N_2O_4 in the organic solvent solution of N_2O_5 can readily be converted to N_2O_5 by treating the solution with ozone. >



Conveniently the N_2O_5 solution could be stored for further use under an ozone containing atmosphere or at a reduced temperature as a result of the tendency of N_2O_5 to degrade over time.

The preferred organic solvent for use in the process of the present invention is dichloromethane but other suitable inert organic solvents such as halon (CFC) substitutes or acetonitrile may be used instead.

Effluent N_2O_4 (containing residual N_2O_5 in solution remaining after recovery of N_2O_5 may be recycled to the anolyte stream to maintain a high level of N_2O_4 therein especially if not prejudicially contaminated by organic compounds. At least some effluent N_2O_4 may, however, be added to the divided portion of the anolyte stream, as described previously.

The overall process may therefore be operated such that there is substantially no output N_2O_4 waste such as to contribute an effluent stream requiring costly recovery processes.

The separated HNO_3 solvent phase may also be returned to the anolyte stream. This substantially does away with any HNO_3 waste effluent stream and any associated necessity for recovery.

N_2O_5 may then be obtained from the separated N_2O_4 phase by further cooling whereupon substantially pure N_2O_5 crystallises out of solution. In consequence of the high thermal solubility gradient found where N_2O_4 is the effective solvent, the proportion of N_2O_5 which may be recovered in a substantially pure form is high. This may then be separated off from the residual N_2O_4 mother liquor and dissolved in a suitable organic solvent. In this manner solutions of N_2O_5 in organic solvents may be obtained which are substantially purer in terms of





contaminants than those which can be obtained by either direct dissolution of the N_2O_5 generated by the Russian process described above or by direct extraction from N_2O_5/HNO_3 mixtures.

According to a third aspect of the present invention there is provided apparatus for use in a process for producing a solution of N_2O_5 in an organic solvent comprising:

an electrochemical cell providing respective anode and cathode compartments having a respective anode and cathode, the compartments being capable of having respective first, anolyte and second, catholyte, streams of N_2O_4 in HNO_3 passed therethrough, said cell further having means for applying a potential difference between the anode and the cathode whereby, in use, an electric current passes through the cell and N_2O_5 is formed electrochemically in the anode compartment, characterised in that the apparatus further comprises:

means for dividing off a portion of the anolyte stream and means for cooling the divided portion to produce a first N_2O_4 solvent phase containing N_2O_5 and a second HNO_3 solvent phase;

a separator for separating the two phases; and

means for recovering N_2O_5 from the first N_2O_4 Phase into an organic solvent to produce a solution of N_2O_5 therein.

Advantageously, the apparatus further comprises means for injecting a stream of N_2O_4 into the divided portion prior to cooling the said portion. In a yet further aspect, the cooling means may be omitted and the apparatus comprise only means for injecting a stream of N_2O_4 into the divided portion so as to produce a first N_2O_4



solvent phase containing N_2O_5 and a second HNO_3 solvent phase.

In general, it will be appreciated that a substantial range of variation in the degree of N_2O_5 partition between the two phases may be obtained by addition of a requisite quantity of liquid N_2O_4 accompanied by efficient mixing and either with or without subsequent cooling.

The present invention will now be described by way of example only, with reference to the accompanying drawings in which:

Figure 1 is an outline phase diagram of the HNO_3 - N_2O_4 - N_2O_5 system;

Figure 2 is a schematic process flow diagram of the method of the invention, and

Figure 3 is a simplified outline phase diagram derived from Figure 1 but showing additionally a typical operation according to the method of the invention.

A series of experiments was conducted to establish the phase diagram illustrated in Figure 1.

Experiment 1

N_2O_4 was added to HNO_3 progressively and with thorough mixing at a temperature of 15°C until the solution became hazy, indicating incipient phase separation. The proportions of the two ingredients at this point are recorded in Table 1.

Experiments 2 to 5

Four solutions of N_2O_5 in HNO_3 were prepared gravimetrically to different strengths at 15°C and N_2O_4 was then added progressively with thorough mixing until

the solutions became hazy, indicating incipient phase separation (whether liquidus, as in nearly all cases, or solidus). The proportions of the three ingredients at this point are recorded for each run in Table 1.

Experiments 6 to 11

The experimental procedure of Experiments 2 to 5 was repeated with a further six solutions but at a temperature of -15°C . The resulting data are again set out in Table 1.

Experiment 12

The experimental procedure of Experiment 1 was repeated except that in this case HNO_3 was added to N_2O_4 until the solution became hazy. The concentrations of the two species at this point are given in Table 1.

Experiments 13 to 16

Four solutions of N_2O_5 in N_2O_4 were prepared gravimetrically to different strengths at a temperature of 15°C and HNO_3 was then added to each solution progressively until the solutions became hazy indicating incipient phase separation. The relative proportions of the three ingredients at this point are recorded for each of the solutions in Table 1.

Experiments 17 and 18

The experimental procedure of Experiments 13 to 16 was repeated with a further two solutions of N_2O_5 in N_2O_4 but at a temperature of -15°C . The proportions at the point of incipient phase separation for each of the solutions are set out in Table 1.



TABLE 1

Expt	Temperature	wt% N_2O_5 in solution	wt% HNO_3 in solution	wt% N_2O_4 in solution
1	+15°C	0	36	64
2	"	7	42	51
3	"	13	47	40
4	"	20	47	33
5	"	24	45	31
6	-15°C	6	50	44
7	"	6	51	43
8	"	13	51	36
9	"	18	50	32
10	"	19	51	30
11	"	26	50	24
12	+15°C	0	8	92
13	"	8	8	84
14	"	20	7	73
15	"	25	7	68
16	"	27	0	73
17	-15°C	11	5	84
18	"	12	0	88

Summary of Experiments

The results of Experiments 1 to 18 are shown plotted on the phase diagram of Figure 1. The data points are respectively designated as points A to R. Additional point S which is known to represent the meeting point of the solidus and liquidus lines at 25°C is taken from the phase diagram which is Figure 1 of UK Patent No. 2 245 266 in the name of one of the co-applicants.

It will be seen from the phase diagram of Figure 1 that two liquid phases can occur, and can be in equilibrium with each other and with a solid N_2O_5 phase. For compositions with a high proportion of HNO_3 , represented by the region towards the top of graph of Figure 1, a dense single liquid phase exists with HNO_3 as the major solvent and this conveniently forms the anolyte for the described process. As the N_2O_4 component

increases, a liquidus curve is reached which represents the saturation of the minor solvent (N_2O_4). Beyond this curve a lighter second liquid phase is formed with N_2O_4 as the major solvent. This phase is in equilibrium with the heavier HNO_3 phase and is represented by the region towards the lower left hand portion of the graph. Thus the data points A to E lie on the liquidus curve for $+15^\circ\text{C}$ and represent the maximum concentration of N_2O_4 in the acid phase at that temperature and for different N_2O_5 concentrations. Beyond point E the liquidus curve intersects with a solidus curve where solvate N_2O_5 crystallises out.

Likewise, data points F to J lie on the liquidus curve for -15°C , with point K lying on the solidus at that temperature such that the intersection of the two curves lies in the region between points J and K. Data point S represents the actual intersection of liquidus and solidus at a temperature of $+25^\circ\text{C}$.

It will be appreciated that the preferred composition for the anolyte in the process of the present invention lies between the curves for $+25^\circ\text{C}$ and -15°C and preferably close to the $+15^\circ\text{C}$ curves near to the point of intersection, since this area provides the maximum concentrations of both N_2O_4 and N_2O_5 that can exist in the anolyte before crystallisation or liquid phase separation. In practice the optimum anolyte composition will lie above the saturation curves for the temperature of operation in order to maintain a safety factor to prevent crystallisation of N_2O_5 occurring on cooling surfaces or premature liquid phase separation.

A second liquid phase can also co-exist with the HNO_3 phase, and is shown by the region in the lower left portion of the phase diagram beyond the curves defined by data points M to O, these representing the approximate position of the saturation (liquidus) curve at $+15^\circ\text{C}$.



This liquidus intersects with the solidus arc beyond point O and point P lies on the solidus and represents the saturation limit for N_2O_5 in N_2O_4 at $+15^\circ\text{C}$. A similar intersection of the liquidus and the solidus curves occurs beyond point Q for -15°C with point R in this case illustrating the saturation of N_2O_5 in N_2O_4 at that temperature.

Referring now to Figure 2 of the drawings, apparatus, generally designated 1, for use in a process for producing a solution of N_2O_5 in an organic solvent comprises an electrochemical cell 2 providing respective anode and cathode compartments 10, 20 having a respective anode and cathode (not shown).

The anode compartment 10 forms part of an anolyte loop 11 having an anolyte storage compartment 12 containing $\text{N}_2\text{O}_5/\text{HNO}_3/\text{N}_2\text{O}_4$. The anode compartment 10 is capable of having a first, anolyte stream of $\text{N}_2\text{O}_5/\text{HNO}_3/\text{N}_2\text{O}_4$ passed therethrough from the anolyte storage compartment 12 via the anolyte loop 11.

The cathode compartment 20 forms part of a catholyte loop 21 having a catholyte storage compartment 22 containing $\text{N}_2\text{O}_4/\text{HNO}_3/\text{water}$. The cathode compartment 20 is capable of having a second, catholyte stream of $\text{N}_2\text{O}_4/\text{HNO}_3/\text{water}$ passed therethrough from the catholyte compartment 22 via the catholyte loop 21.

An explanation of the functioning of such electrochemical cells can be found in UK Patent No. 2 245 003. Essentially, a first, anolyte stream of $\text{N}_2\text{O}_5/\text{HNO}_3/\text{N}_2\text{O}_4$ is passed through the anode compartment 10, and a second, catholyte stream of $\text{water}/\text{HNO}_3/\text{N}_2\text{O}_4$ passed through the cathode compartment 20 whilst applying a potential difference between the anode and the cathode.



In this way electrical current is passed through the cell 2 and N_2O_5 electrochemically formed in the anode compartment 10.

It is envisaged that, in use, the catholyte loop 21, would initially contain concentrated (typically 98%) HNO_3 but would build up a considerable concentration of water and N_2O_4 during the electrolysis. During operation of the process small quantities of the catholyte stream would be removed in a continuous manner and the catholyte stream replenished with fresh HNO_3 . The material removed would be treated to remove water as dilute HNO_3 residual substantially water-free HNO_3 and N_2O_4 being recycled.

The anolyte loop 11 contains the anolyte, which would initially be N_2O_4 in HNO_3 but would build up to a steady state (under extraction conditions) containing at least 15% and 20% respectively of N_2O_5 and N_2O_4 (by weight), during electrolysis depending on the temperature of the anolyte.

It is further envisaged that the electrochemical cell 2 would employ a cationic exchange membrane such as NAFION 324 or NAFION 350 which are proprietary materials manufactured by Messrs DuPont de Nemours. In the present process, the concentration of N_2O_4 in the anolyte is greater than 20% w/w so that a cation exchange membrane can be used without incurring an unacceptably low efficiency.

The apparatus further provides means by which a minor portion (say between 1% and 20%) of the $N_2O_5/HNO_3/N_2O_4$ anolyte stream can be divided off from the rest of the anolyte stream: the divided portion is shown as 31 on Figure 1. By dividing off only a small proportion of the anolyte for further treatment, the main electrochemical process can be operated in a continuous manner under constant steady state conditions and



solute/solvent equilibrium can be maintained throughout. Moreover, by using a continuous separation process it is only necessary to remove a relatively small proportion of the solute, N_2O_5 and since phase separation into N_2O_4 and HNO_3 phases occurs under essentially equilibrium conditions elaborate countercurrent methods involving mass transfer of solute are not required. It will be appreciated then that the application of the continuous process of separation to the continuous output from the electrolytic process provides a highly economical procedure overall and one which is well suited to an industrial process.

The apparatus also provides a mixer 32 to which the minor portion is passed, and in which further N_2O_4 may be introduced into the minor portion. Thereafter the minor portion (with or without added N_2O_4) may be cooled to a temperature of around $-5^\circ C$ to $+15^\circ C$ using the cooler 33.

The apparatus also provides a separator 34 to which the (optionally cooled) solution or mixture is then passed. The separator 34 allows the minor portion to separate into two parts, namely an upper N_2O_4 layer containing N_2O_5 and small amounts of HNO_3 and a lower HNO_3 layer containing both N_2O_5 and N_2O_4 .

The separator 34 may additionally include cooling means whereby the minor portion may be maintained at the desired temperature so as to promote the formation of the upper and lower layers and take off means by which the upper and lower layers may be made remote from one another.

There is further provided abstracting means, in this embodiment, in the form of a crystalliser 41 to which the upper N_2O_4 layer is passed. In the crystalliser 41 the N_2O_4 layer is chilled to induce N_2O_5 precipitation. Because at lower temperatures the viscosity of the



mixture becomes too high to allow satisfactory separation of the crystalline N_2O_5 from the liquor, a temperature of $-15^{\circ}C$ represents a practicable lower limit for operation of crystalliser 41.

The N_2O_5 crystals obtained from the crystalliser are only slightly contaminated with HNO_3 and N_2O_4 and can thence be removed and redissolved in a suitable organic solvent, such as dichloromethane.

The HNO_3 solvent phase produced by the separator 34 is recycled by return to the anolyte loop 11.

Further, effluent N_2O_4 remaining after abstraction of N_2O_5 from the N_2O_4 layer is recycled by feeding to an N_2O_4 storage tank 42, from which tank 42 the divided portion 31 may be injected with N_2O_4 in the mixer 32 in an amount sufficient to saturate the portion prior to separation thereof in the separator 34, as previously explained.

Such recycling of what would otherwise be classed as waste streams obviates the need to dispose of such, and provides an associated cost advantage.

The particular advantage of the process described herewith may be said to depend on the fact that the HNO_3 phase has a high temperature solubility coefficient with respect to N_2O_4 but a lower coefficient with respect to N_2O_5 which permits a rapid separation of the liquid phases without crystallization of solid N_2O_5 when there is a small reduction in temperature of the mixture and that the N_2O_4 phase has both a low content and low coefficient of solubility of HNO_3 but a high coefficient in respect of N_2O_5 thus permitting the rapid and easy formation of relatively pure N_2O_5 crystals on reducing the temperature of this phase. Hence a two stage reduction in temperature with an intermediate phase separation stage will effect transfer of the N_2O_5 from a saturated single





phase three component mixture into a solution in N_2O_4 from which it is readily crystallizable in an essentially pure form which is suitable for re-solution in a suitable organic solvent.

Operation of the process of this present invention may now be exemplified in the following manner.

Example 1

Based on a process of operating an electrochemical cell to generate N_2O_5 in a mixture of N_2O_4 and HNO_3 in accordance with known procedures (see UK Patent No. 2 245 003), synthetic mixtures of all three components were prepared and mixed thoroughly before being each allowed to separate into two layers which were then isolated. The synthetic mixtures each replicated a product of such an electrochemical cell to which N_2O_4 had been added and which had been cooled to a temperature of $15^\circ C$. After separation, samples of each layer were analysed to provide the composition of the upper and lower phases. The results are given in Table 2.

TABLE 2

%w/w in mixture N_2O_4 N_2O_5 HNO_3			%w/w in upper layer N_2O_4 N_2O_5 HNO_3			%w/w in lower layer N_2O_4 N_2O_5 HNO_3		
47	19	34	75	17	8	36	20	44
46	22	32	71	20	9	30	23	47

Example 2

A synthetic mixture with a composition corresponding approximately to that of the upper layers obtained in Example 1 was prepared gravimetrically. The mixture was then chilled to yield crystals which were filtered off and washed with cold dichloromethane. Analyses of the



original synthetic mixture and of the crystalline product obtained before and after washing are given in Table 3.

TABLE 3

%w/w original mixture N ₂ O ₄ N ₂ O ₅ HNO ₃	%w/w wet crystals N ₂ O ₄ N ₂ O ₅ HNO ₃	%w/w washed crystals N ₂ O ₄ N ₂ O ₅ HNO ₃
68 28 4	8 87 5	0 100 0

The processes described in Examples 1 and 2 and in relation to the process flow diagram of Figure 2 may now be further explained with reference to Figure 3 which shows a simplified representation of the phase diagram of Figure 1 with the solidi and liquidus of that diagram only drawn in. In addition, the phase diagram of Figure 3 shows certain tie lines which connect the compositions of two liquid phases co-existing in equilibrium. Such liquid phases in equilibrium are possible where the respective compositions at a given temperature each lie on one of the two liquidus for that temperature.

For example, data points A and L on the left hand axis of the diagram of Figure 1 represent two compositions which are in equilibrium and which are connected by a tie line lying along the left hand axis. Moving to compositions further to the right on each liquidus, those pairs of compositions which are in equilibrium will be indicated by tie lines which lie broadly parallel to the left hand axis, their exact disposition reflecting the preferential uptake of the solute N₂O₅ in one of the solvent phases.

Point V represents a typical anolyte composition for operation of an electrochemical cell at +15°C, ie with ca. 30 wt% N₂O₄ and ca. 23 wt% N₂O₅. Injection into this composition of N₂O₄ (with efficient mixing) is represented by movement in the direction of the arrow along the line VV', the composition V' corresponding to the composition

of the mother liquor which remains after ultimate crystallisation of N_2O_5 . Dependent on the respective quantities of added N_2O_4 and of the minor portion of the anolyte of composition V, the mixture may be said to reach a composition represented on the diagram of Figure 3 by point W. This, in the embodiment chosen, represents a composition with ca. 46 wt% N_2O_4 and ca. 19 wt% N_2O_5 , that is, of roughly the same composition as the mixtures of Example 1.

Composition W is not a stable mixture and on being allowed to divide will form two phases or layers with compositions represented by respective points W' and W" lying on the two liquidi at either end of the tie line W'W". From this point the two layers are separated and the heavier acid layer represented by point W' is returned back to the anolyte loop (as previously described in connection with Figure 2), while the composition W", in which N_2O_4 is the solvent, is fed to the chiller and crystalliser. The compositions at W' and W" correspond approximately to those of the two layers produced in Example 1 (Table 2).

When the N_2O_4 solvent layer (W") is cooled, solid pure N_2O_5 crystallises out as indicated by line W'X'. As N_2O_5 crystallises out (ie a composition represented by X'), the remaining N_2O_4 layer becomes enriched with respect to N_2O_4 as represented by a composition at point X. This composition is again unstable and the result could be a further separation to compositions represented by points Y and Y' (shown this time as lying at either end of tie line YY' on the respective liquidi at -15°C , because of the cooling of the liquid). In practice any separate HNO_3 which may arise (ie. composition Y) will be entrained in the major N_2O_4 phase (composition Y') and will be returned to the earlier part of the process via the N_2O_4 storage tank 42 (Figure 2).



THIS SHEET HAS BEEN
REPLACED

In summary, for a given anolyte composition V, the quantity of N_2O_5 extracted is controlled by the flow rate of the anolyte loop take-off, by the quantity of N_2O_4 liquor mixed with it, and by the relative temperatures of the separation stage and the crystalliser.

This Sheet Has Been Replaced



CLAIMS

1. A process for producing a solution of N_2O_5 in an organic solvent comprising the steps of:

passing anolyte and catholyte streams of N_2O_4 in HNO_3 through respective anode and cathode compartments of an electrochemical cell whilst applying a potential difference between an anode and a cathode thereof, whereby electrical current is passed through the cell and N_2O_5 is electrochemically formed in the anode compartment, characterised by the further steps of:

dividing off a portion of the anolyte stream and causing the divided portion to separate to produce a first N_2O_4 solvent phase containing N_2O_5 and a second HNO_3 solvent phase also containing N_2O_5 ;

separating the two phases in a separator; and

recovering N_2O_5 from the first N_2O_4 phase into an organic solvent to produce a solution of N_2O_5 therein.

2. A process for producing a solution of N_2O_5 in an organic solvent comprising the steps of:

passing anolyte and catholyte streams of N_2O_4 in HNO_3 through respective anode and cathode compartments of an electrochemical cell whilst applying a potential difference between an anode and a cathode thereof, whereby electrical current is passed through the cell and N_2O_5 is electrochemically formed in the anode compartment, characterised by the further steps of:

dividing off a portion of the anolyte stream, saturating the divided portion with N_2O_4 by addition thereto of N_2O_4 with thorough mixing, to produce a first



N₂O₄ solvent phase containing N₂O₅ and a second HNO₃ solvent phase also containing N₂O₅;

separating the two phases in a separator; and

recovering N₂O₅ from the first N₂O₄ phase into an organic solvent to produce a solution of N₂O₅ therein.

3. A process according to claim 2, wherein, after addition of N₂O₄ to the divided portion, the portion is cooled.

4. A process according to claim 3, wherein the portion is cooled to a temperature of between -5 and +15°C.

5. A process according to any one of claims 1 to 4, wherein the concentration of N₂O₄ in the anolyte stream is maintained at at least 20 weight%.

6. A process according to claim 5, wherein the concentration is maintained at at least 30 wt%.

7. A process according to any of claims 1 to 6 wherein the concentration of N₂O₅ in the anolyte stream is maintained at at least 15 wt%.

8. A process according to claim 7, wherein the concentration is maintained at at least 20 wt%.

9. A process according to any one of the preceding claims, wherein the temperature of the anolyte stream exiting from the electrochemical cell is maintained in the range of 0 to 30°C.

10. A process according to any one of the preceding claims wherein the portion of the anolyte stream which is divided off is a minor portion thereof.



* C L M S *

This Sheet Has Been Replaced



11. A process according to claim 10, wherein the minor portion comprises from 1 to 20 wt% of the anolyte stream.

12. A process according to claim 11, wherein the minor portion comprises approximately 5 wt% of the anolyte stream.

13. A process according to any one of the preceding claims, wherein the N_2O_5 product is recovered from the first N_2O_4 phase by chilling the N_2O_4 phase to induce crystallization either in bulk or on a cold surface and then respectively filtering off the solid or draining the liquid phase from the surface, followed by re-dissolving the solid N_2O_5 in an organic solvent.

14. A process according to any one of claims 1 to 12, wherein the N_2O_5 product is recovered from the first N_2O_4 phase by applying reduced pressure to the N_2O_4 phase to cause the solvent N_2O_4 to be distilled off and re-dissolving the N_2O_5 produced in an organic solvent.

15. A process according to any one of claims 1 to 12, wherein the N_2O_5 product is recovered from the first N_2O_4 phase by feeding the N_2O_4 phase directly into an organic solvent and subjecting the mixture to fractional distillation at reduced pressure to remove the volatile N_2O_4 leaving a solution of N_2O_5 in the organic solvent.

16. A process according to any one of the preceding claims wherein the organic solvent is dichloromethane or acetonitrile.

17. Apparatus for use in a process for producing a solution of N_2O_5 in an organic solvent, which apparatus comprises:



This Sheet Has Been Replaced



an electrochemical cell providing respective anode and cathode compartments having a respective anode and cathode, the compartments being capable of having respective first, anolyte and second, catholyte, streams of N_2O_4 in HNO_3 passed therethrough, said cell further having means for applying a potential difference between the anode and the cathode whereby, in use, an electric current passes through the cell and N_2O_5 is formed electrochemically in the anode compartment, characterised in that the apparatus further comprises:

means for dividing off a portion of the anolyte stream and means for cooling the divided portion to produce a first N_2O_4 solvent phase containing N_2O_5 and a second HNO_3 solvent phase;

a separator for separating the two phases; and

means for recovering N_2O_5 from the first N_2O_4 phase into an organic solvent to produce a solution of N_2O_5 therein.

18. Apparatus according to claim 17 and further comprising means for injecting a stream of N_2O_4 into the divided off portion of the anolyte stream prior to cooling the portion.

19. Apparatus according to claim 17 or 18, wherein effluent N_2O_4 remaining after recovery of N_2O_5 from the N_2O_4 phase is recycled to the anolyte stream of the electrochemical cell.

20. Apparatus according to claim 19, wherein at least a part of the effluent N_2O_4 is recycled to be injected into the divided portion of the anolyte stream.



THIS SHEET HAS BEEN
REPLACED

21. Apparatus according to any of claims 17 to 20,
wherein the separated HNO_3 solvent phase is returned to
the anolyte stream of the electrochemical cell.

This Sheet Has Been Replaced



* C L M S *

ABSTRACT

SOLVENT TRANSFER PROCESS FOR DINITROGEN PENTOXIDE

A process for the production of dinitrogen pentoxide (N_2O_5) in an organic solvent consists of dividing off a minor proportion (31) of the anolyte stream (11) of an electrolytic cell (2) which is set up to generate N_2O_5 and of cooling that portion and/or adding to the portion a quantity of N_2O_4 , such that two phases are formed. The phases are separated (34) and the light (upper) N_2O_4 phase is then stripped of dissolved N_2O_5 , the N_2O_5 being redissolved in an organic solvent. Conveniently, the N_2O_4 phase is chilled (at 41) to produce crystalline N_2O_5 which is dissolved in an organic solvent such as dichloromethane. All effluent streams may be recycled with addition only of fresh concentrated nitric acid and fresh N_2O_4 to make the process capable of continuous operation.

This Sheet Has Been Replaced



Fig.1.

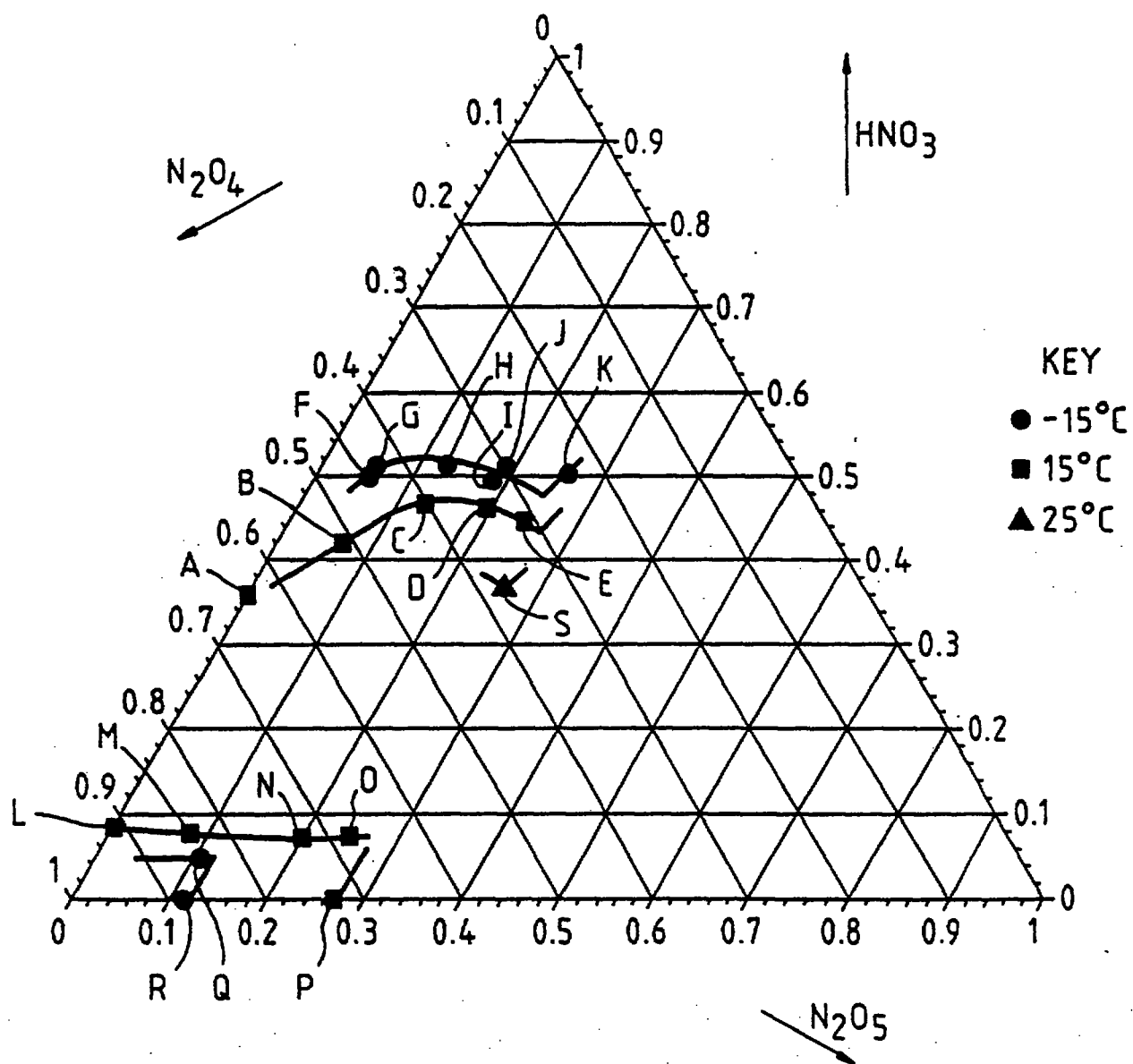


Fig.2.

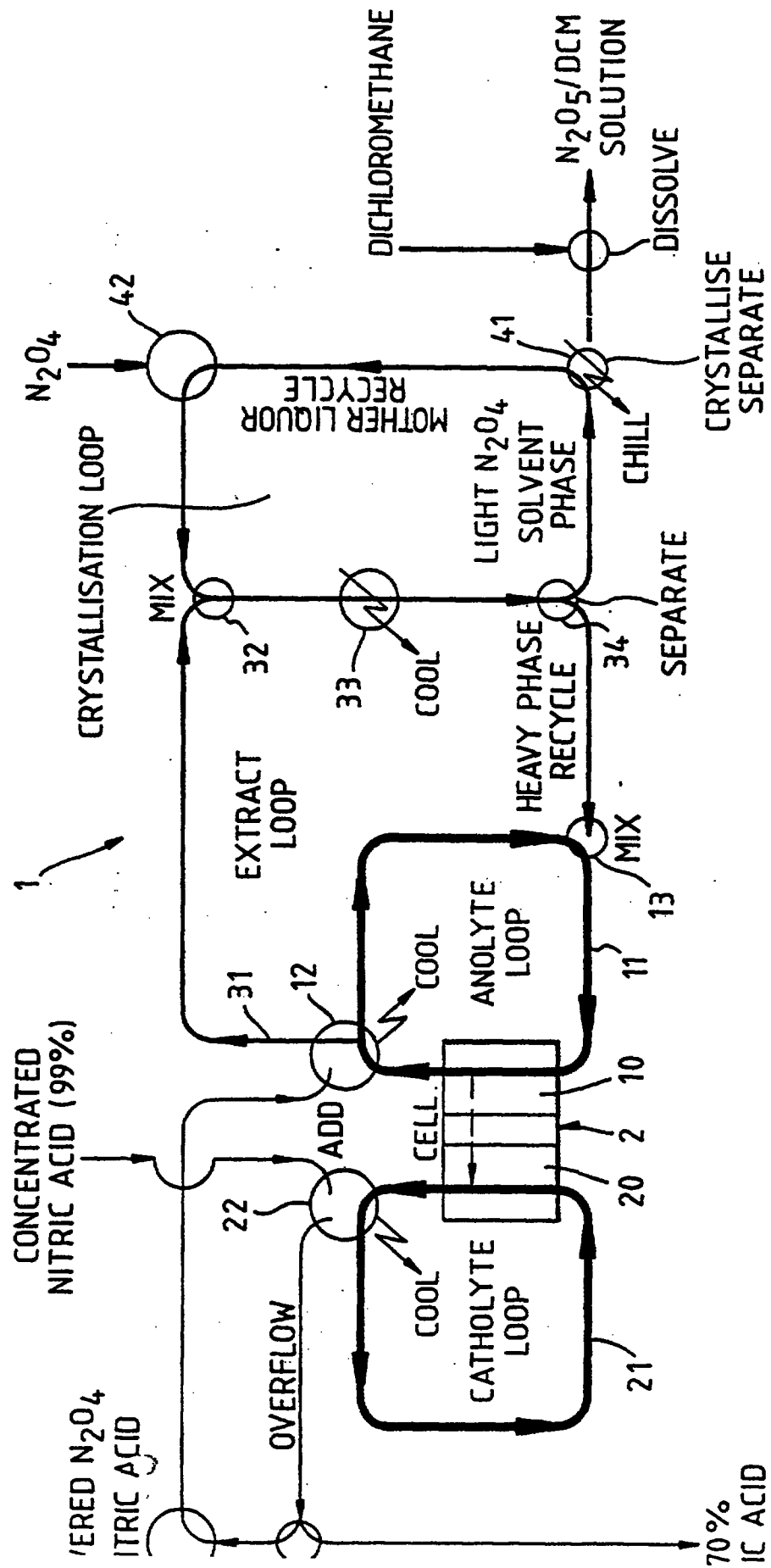
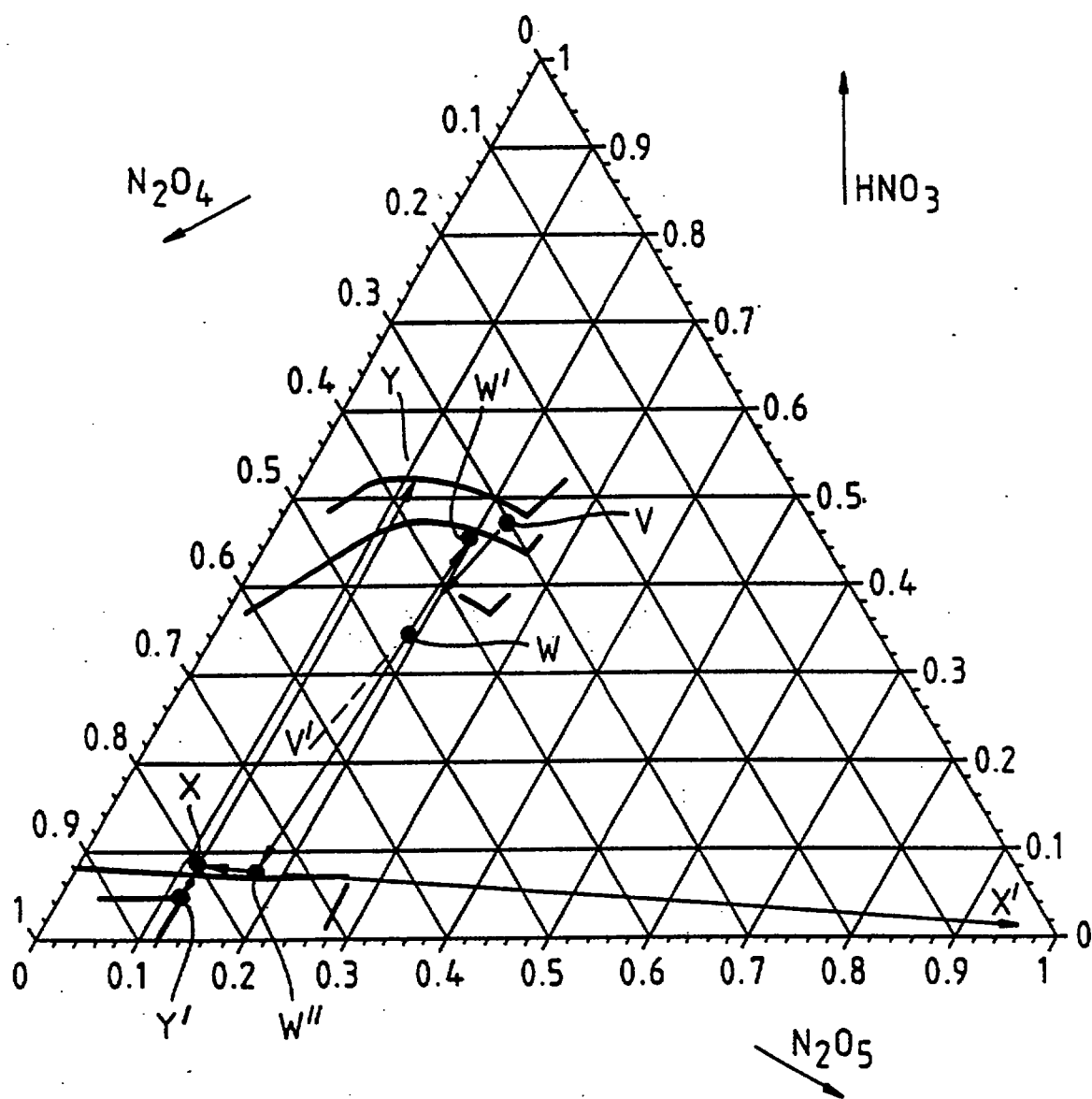


Fig.3.



2-6381000

Abstract

A process for the production of dinitrogen pentoxide (N_2O_5) in an organic solvent consists of dividing off a minor proportion (31) of the anolyte stream (11) of an electrolytic cell (2) which is set up to generate N_2O_5 and of cooling that portion and/or adding to the portion a quantity of N_2O_4 , such that two phases are formed. The phases are separated (34) and the light (upper) N_2O_4 phase is then stripped of dissolved N_2O_5 , the N_2O_5 being redissolved in an organic solvent. Conveniently, the N_2O_4 phase is chilled (at 41) to produce crystalline N_2O_5 which is dissolved in an organic solvent such as dichloromethane. All effluent streams may be recycled with addition only of fresh concentrated nitric acid and fresh N_2O_4 to make the process capable of continuous operation.

FIGURE 2

8-0801489

Date: 17 FEB 1998

SOLVENT TRANSFER PROCESS FOR DINITROGEN PENTOXIDE

This invention relates to a process for the recovery of dinitrogen pentoxide, N_2O_5 , from an anolyte loop of an electrochemical cell into an alternative solvent system.

It is known to produce N_2O_5 by an electrochemical process. Such a process is described in GB Patent No. 2 245 003 in the name of one of the co-applicants.

Overall, such a process involves the conversion of HNO_3 to N_2O_5 and water, with N_2O_4 playing a role in the electrochemical reactions. The product is N_2O_5 in solution in HNO_3 with a small amount of N_2O_4 impurity. The concentration of N_2O_5 in this product is typically around 32 wt.% which is close to the saturation point for this solute/solvent system.

The importance of N_2O_5 has recently increased due to its application in the synthesis of energetic compounds, and particularly energetic polymers such as poly(3-nitratomethyl-3-methyloxetane) (polyNIMMO) or Polyglycidyl nitrate (PolyGLYN).

For use in organic nitration processes it is desirable that the N_2O_5 should be available in an inert organic solvent, such as dichloromethane. This could be achieved by solvent extraction from an HNO_3 solution. However such a process would be prohibitively costly to construct and operate, requiring substantial fixed plant. There would also be a likelihood of back-contamination of any electrolytic circuit by the organic solvent through recycling of the HNO_3 .

It is known from USSR Inventor's Certificate SU-1089047A that solid N_2O_5 can be separated from strong 35-40 wt.% solutions of N_2O_5 in nitric acid by the addition of moderate amounts of N_2O_4 at a temperature of -5 to 0°C.

Date 17 FEB 1998

This results in precipitation of N_2O_5 contaminated with considerable amounts of HNO_3 from the solution. The presence of HNO_3 in this solid N_2O_5 makes it unsuitable for use in specific organic nitration procedures involving acid sensitive substrates. Relatively pure N_2O_5 can be obtained from this solid material by low pressure sublimation and subsequent condensation onto a cold surface. The overall procedure, however, then becomes lengthy and cumbersome and as such not suited to an industrial process. Moreover, this method of N_2O_5 production requires a starting solution of N_2O_5 in HNO_3 which is electrochemically less efficient and more costly to produce because of the very low proportion of N_2O_4 which it must contain.

In UK Patent No. 2 245 266 in the name of one of the co-applicants, there is disclosed a method of N_2O_5 separation, wherein a solution of N_2O_5 in HNO_3 at a temperature of at least $10^\circ C$ (and containing at least 45 weight percent of dissolved N_2O_4 and N_2O_5 and further having a dissolved N_2O_5 : HNO_3 ratio by weight of at least 1:3) is cooled to less than $8^\circ C$ until an N_2O_5 solvate precipitates from the solution. The disclosure teaches that formation of a separate liquid N_2O_4 Phase is to be avoided since this reduces the yield of N_2O_5 solvate, with a proportion of the N_2O_5 instead entering the liquid N_2O_4 phase. This is particularly true for temperatures below about 0 to $-5^\circ C$, at which the N_2O_4 tends more readily to form a separate liquid phase.

It has been found that if the N_2O_5/HNO_3 mixture obtained from the electrochemical process for producing N_2O_5 is maintained at or near saturation with N_2O_4 and then cooled, phase separation takes place in which N_2O_4 is the principal solvent of one phase and HNO_3 the principal solvent of the other phase. N_2O_5 is present within, and in equilibrium between, the two phases. The two phases may be readily separated and the N_2O_5 in the N_2O_4 phase can

be efficiently extracted therefrom. The N_2O_5 extracted from the N_2O_4 phase can then be taken up into a suitable organic solvent either directly by extraction or by dissolution following isolation of solid N_2O_5 ". It has been found that N_2O_5 can be produced in an organic solvent in a more pure form than has previously been achieved through extraction from a (mainly) nitric acid solution as described above.

Further, it has been found that by using only a small proportion of the recirculating anolyte stream of the electrochemical process, N_2O_5 can be effectively stripped out of the mixture on a continuous basis without disrupting the steady state operation of the electrochemical process.

Accordingly, a first aspect of the present invention provides a process for producing a solution of N_2O_5 in an organic solvent, comprising the steps of:

passing anolyte and catholyte streams of N_2O_4 in HNO_3 through respective anode and cathode compartments of an electrochemical cell whilst applying a potential difference between an anode and a cathode thereof, whereby electrical current is passed through the cell and N_2O_5 is electrochemically formed in the anode compartment, characterised by the further steps of:

dividing off a portion of the anolyte stream and causing the divided portion to separate to produce a first N_2O_4 solvent phase containing N_2O_5 and a second HNO_3 solvent phase also containing N_2O_5 ;

separating the two phases in a separator; and

recovering N_2O_5 from the first N_2O_4 phase into an organic solvent, to produce a solution of N_2O_5 therein.

17 FEB 1998

Date :

The electrolytic process should preferably be operated at a maximum possible temperature which is consistent with the need to avoid decomposition of the materials involved.

An exit temperature for the anolyte stream in the range of 0 - 30°C is preferable, more preferably in the range 15 - 25°C. By this means it may be sought to optimise the efficiency of the overall process of the invention since the higher the temperature of the starting solution, that is the anolyte stream, the greater can be the quantity of N_2O_3 and N_2O_4 dissolved and therefore the greater will be the quantity of N_2O_3 in the final separated N_2O_4 Phase and so available for crystallisation.

Preferably, the electrochemical process should operate with the anolyte stream close to saturation with respect to N_2O_4 , the concentration of N_2O_4 typically being at least 20 wt%, and preferably, at least 30 wt% of the anolyte stream.

The divided portion of the anolyte stream may be caused to separate into two phases either by cooling or by addition thereto of N_2O_4 such that the divided portion becomes over saturated with respect to N_2O_4 . Addition of further N_2O_4 in this way also has the advantage of increasing the volume of the separated N_2O_4 layer and hence the amount of N_2O_3 which may be removed from the system as product.

The added N_2O_4 may consist of fresh liquid N_2O_4 recovered/recycled N_2O_4 from a previous recovery processs, or a combination of both.

Alternatively, a combination of addition of N_2O_4 with cooling may be used to cause two liquid phases to form. In this case it is preferred to add N_2O_4 to the divided

Date: 17 FEB 1998

portion of the anolyte stream before the portion passes to the separator in order to ensure that the portion is saturated with N_2O_4 prior to cooling.

According to a second aspect of the present invention there is provided a process for producing a solution of N_2O_5 in an organic solvent comprising the steps of:

passing anolyte and catholyte streams of N_2O_4 in HNO_3 through respective anode and cathode compartments of an electrochemical cell whilst applying a potential difference between an anode and a cathode thereof, whereby electrical current is passed through the cell and N_2O_5 is electrochemically formed in the anode compartment, characterised by the further steps of:

dividing off a portion of the anolyte stream, saturating the divided portion with N_2O_4 by addition thereto of N_2O_4 with thorough mixing, to produce a first N_2O_4 solvent phase containing N_2O_5 and a second HNO_3 solvent phase also containing N_2O_5

separating the two phases in a separator; and

recovering N_2O_5 from the first N_2O_4 Phase into an organic solvent to produce a solution of N_2O_5 therein.

Preferably the process further comprises cooling the divided portion subsequent to its saturation with N_2O_4 .

It is worth noting that use of such essentially simple variables to control the process of the present invention emphasises the advantage of the present process over more elaborate counter-current type extraction processes.

17 FEB 1990

Date :

Where two phases are produced simply by cooling the divided portion of the anolyte stream, because partitioning of the N_2O_5 is taking place from an homogeneous solution, the proportion of N_2O_5 in the two phases is instantaneously in the equilibrium proportion making the partition more efficient than that of simple solvent extraction where mass transfer considerations must be taken into account. Even where excess N_2O_5 is added to the divided portion of the anolyte stream (and either with or without subsequent cooling), such that the partition which occurs is not strictly under equilibrium conditions, in practice the results are essentially very similar, provided the addition takes place with efficient mixing. It is necessary that where the divided portion is to be cooled, it should have been thoroughly mixed beforehand.

Where the divided portion is cooled, this should be to a temperature of around -5 to $+15^\circ\text{C}$.

Further, the process should preferably operate with the anolyte stream close to saturation with respect to N_2O_5 compatible with the avoidance of crystallization of N_2O_5 in the anolyte stream. Typically, the concentration of N_2O_5 will be at least 15 wt% and preferably at least 20 wt%.

The electrochemical cell preferably employs a cationic exchange membrane (such as that described in UK Patent No. 2 245 003 in the name of one of the co-applicants), so that increases in the mass of HNO_3 in the anolyte stream by intra-cell transfer from the catholyte is avoided. Use of an anionic membrane would allow HNO_3 to pass through from catholyte to anolyte such as to effectively render continuous operation of the electrochemical and phase separation processes uneconomic.

Preferably the divided portion of the anolyte stream is a minor portion thereof. This allows the cell and process to be operated continuously. The portion of the anolyte stream divided off is advantageously such that, under the conditions of transfer of N_2O_5 which exist downstream, the amount of transferred N_2O_5 will substantially equal the amount of N_2O_5 being generated in the cell. In this way the cell, and hence the process, may be operated in a steady state manner.

Preferably the divided portion is approximately 1 wt% to 20 wt% of the anolyte stream, and more preferably approximately 5 wt% thereof.

Recovery of N_2O_5 from the N_2O_4 Phase may be accomplished in a number of ways, for example, abstraction (extraction) or distillation (evaporation). Possible recovery methods include:

chilling the N_2O_4 phase to induce crystallization either in bulk or on a cold surface and then respectively filtering off the solid or draining the liquid phase from the surface, followed by re-dissolving the solid N_2O_5 in an organic solvent; or

applying reduced pressure to the N_2O_4 phase to cause the solvent N_2O_4 to be distilled off and re-dissolving the N_2O_5 produced in an organic solvent; or

feeding the N_2O_4 phase directly into an organic solvent and subjecting the mixture to fractional distillation at reduced pressure to remove the volatile N_2O_4 , leaving a solution of N_2O_5 in the organic solvent.

Any residual N_2O_4 in the organic solvent solution of N_2O_5 can readily be converted to N_2O_5 by treating the solution with ozone.

Date: 17 FEB 1991

Conveniently the N_2O_5 solution could be stored for further use under an ozone containing atmosphere or at a reduced temperature as a result of the tendency of N_2O_5 to degrade over time.

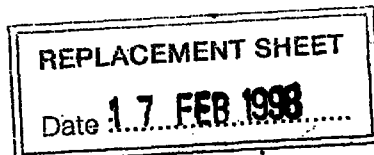
The preferred organic solvent for use in the process of the present invention is dichloromethane but other suitable inert organic solvents such as halon (CFC) substitutes or acetonitrile may be used instead.

Effluent N_2O_4 (containing residual N_2O_5 in solution remaining after recovery of N_2O_5 may be recycled to the anolyte stream to maintain a high level of N_2O_4 therein especially if not prejudicially contaminated by organic compounds. At least some effluent N_2O_4 may, however, be added to the divided portion of the anolyte stream, as described previously.

The overall process may therefore be operated such that there is substantially no output N_2O_4 waste such as to contribute an effluent stream requiring costly recovery processes.

The separated HNO_3 solvent phase may also be returned to the anolyte stream. This substantially does away with any HNO_3 waste effluent stream and any associated necessity for recovery.

N_2O_5 may then be obtained from the separated N_2O_4 phase by further cooling whereupon substantially pure N_2O_5 crystallises out of solution. In consequence of the high thermal solubility gradient found where N_2O_4 is the effective solvent, the proportion of N_2O_5 which may be recovered in a substantially pure form is high. This may then be separated off from the residual N_2O_4 mother liquor and dissolved in a suitable organic solvent. In this manner solutions of N_2O_5 in organic solvents may be obtained which are substantially purer in terms of



contaminants than those which can be obtained by either direct dissolution of the N_2O_5 generated by the Russian process described above or by direct extraction from N_2O_5/HNO_3 mixtures.

According to a third aspect of the present invention there is provided apparatus for use in a process for producing a solution of N_2O_5 in an organic solvent comprising:

an electrochemical cell providing respective anode and cathode compartments having a respective anode and cathode, the compartments being capable of having respective first, anolyte and second, catholyte, streams of N_2O_4 in HNO_3 passed therethrough, said cell further having means for applying a potential difference between the anode and the cathode whereby, in use, an electric current passes through the cell and N_2O_5 is formed electrochemically in the anode compartment, characterised in that the apparatus further comprises:

means for dividing off a portion of the anolyte stream and means for cooling the divided portion to produce a first N_2O_4 solvent phase containing N_2O_5 and a second HNO_3 solvent phase;

a separator for separating the two phases; and

means for recovering N_2O_5 from the first N_2O_4 Phase into an organic solvent to produce a solution of N_2O_5 therein.

Advantageously, the apparatus further comprises means for injecting a stream of N_2O_4 into the divided portion prior to cooling the said portion. In a yet further aspect, the cooling means may be omitted and the apparatus comprise only means for injecting a stream of N_2O_4 into the divided portion so as to produce a first N_2O_4

Date: 17 FEB 1998

solvent phase containing N_2O_5 and a second HNO_3 solvent phase.

In general, it will be appreciated that a substantial range of variation in the degree of N_2O_5 partition between the two phases may be obtained by addition of a requisite quantity of liquid N_2O_4 accompanied by efficient mixing and either with or without subsequent cooling.

The present invention will now be described by way of example only, with reference to the accompanying drawings in which:

Figure 1 is an outline phase diagram of the HNO_3 - N_2O_4 - N_2O_5 system;

Figure 2 is a schematic process flow diagram of an embodiment of the method of the present invention, and

Figure 3 is a simplified outline phase diagram derived from Figure 1 but showing additionally a typical operation according to the embodiment of the method of the present invention of Fig 2.

A series of experiments were conducted to establish the phase diagram illustrated in Figure 1.

Experiment 1

N_2O_4 was added to HNO_3 progressively and with thorough mixing at a temperature of $15^\circ C$ until the solution became hazy, indicating incipient phase separation. The proportions of the two ingredients at this point are recorded in Table 1.

Experiments 2 to 5

Four solutions of N_2O_5 in HNO_3 were prepared gravimetrically to different strengths at $15^\circ C$ and N_2O_4 was then added progressively with thorough mixing until

Date: 17 FEB 1998

the solutions became hazy, indicating incipient phase separation (whether liquidus, as in nearly all cases, or solidus). The proportions of the three ingredients at this point are recorded for each run in Table 1.

Experiments 6 to 11

The experimental procedure of Experiments 2 to 5 was repeated with a further six solutions but at a temperature of -15°C . The resulting data are again set out in Table 1.

Experiment 12

The experimental procedure of Experiment 1 was repeated except that in this case HNO_3 was added to N_2O_4 until the solution became hazy. The concentrations of the two species at this point are given in Table 1.

Experiments 13 to 16

Four solutions of N_2O_5 in N_2O_4 were prepared gravimetrically to different strengths at a temperature of 15°C and HNO_3 was then added to each solution progressively until the solutions became hazy indicating incipient phase separation. The relative proportions of the three ingredients at this point are recorded for each of the solutions in Table 1.

Experiments 17 and 18

The experimental procedure of Experiments 13 to 16 was repeated with a further two solutions of N_2O_5 in N_2O_4 but at a temperature of -15°C . The proportions at the point of incipient phase separation for each of the solutions are set out in Table 1.

TABLE 1

Expt	Temperature	wt% N ₂ O ₅ in solution	wt% HNO ₃ in solution	wt% N ₂ O ₄ in solution
1	+15°C	0	36	64
2	"	7	42	51
3	"	13	47	40
4	"	20	47	33
5	"	24	45	31
6	-15°C	6	50	44
7	"	6	51	43
8	"	13	51	36
9	"	18	50	32
10	"	19	51	30
11	"	26	50	24
12	-15°C	0	8	92
13	"	8	8	84
14	"	20	7	73
15	"	25	7	68
16	"	27	0	73
17	-15°C	11	5	84
18	"	12	0	88

Summary of Experiments

The results of Experiments 1 to 18 are shown plotted on the phase diagram of Figure 1. The data points are respectively designated as points A to R. Additional point S which is known to represent the meeting point of the solidus and liquidus lines at 25°C is taken from the phase diagram which is Figure 1 of UK Patent No. 2 245 266 in the name of one of the co-applicants.

It will be seen from the phase diagram of Figure 1 that two liquid phases can occur, and can be in equilibrium with each other and with a solid N₂O₅ phase. For compositions with a high proportion of HNO₃, represented by the region towards the top of graph of Figure 1, a dense single liquid phase exists with HNO₃ as the major solvent and this conveniently forms the anolyte for the described process. As the N₂O₄ component

Date 17 FEB 1998

increases, a liquidus curve is reached which represents the saturation of the minor solvent (N_2O_4). Beyond this curve a lighter second liquid phase is formed with N_2O_4 as the major solvent. This phase is in equilibrium with the heavier HNO_3 phase and is represented by the region towards the lower left hand portion of the graph. Thus the data points A to E lie on the liquidus curve for $+15^\circ C$ and represent the maximum concentration of N_2O_4 in the acid phase at that temperature and for different N_2O_5 concentrations. Beyond point E the liquidus curve intersects with a solidus curve where solvate N_2O_5 crystallises out.

Likewise, data points F to J lie on the liquidus curve for $-15^\circ C$, with point K lying on the solidus at that temperature such that the intersection of the two curves lies in the region between points J and K. Data point S represents the actual intersection of liquidus and solidus at a temperature of $+25^\circ C$.

It will be appreciated that the preferred composition for the anolyte in the process of the present invention lies between the curves for $+25^\circ C$ and $-15^\circ C$ and preferably close to the $+15^\circ C$ curves near to the point of intersection, since this area provides the maximum concentrations of both N_2O_4 and N_2O_5 that can exist in the anolyte before crystallisation or liquid phase separation. In practice the optimum anolyte composition will lie above the saturation curves for the temperature of operation in order to maintain a safety factor to prevent crystallisation of N_2O_5 occurring on cooling surfaces or premature liquid phase separation.

A second liquid phase can also co-exist with the HNO_3 phase, and is shown by the region in the lower left portion of the phase diagram beyond the curves defined by data points M to O, these representing the approximate position of the saturation (liquidus) curve at $-15^\circ C$.

This liquidus intersects with the solidus arc beyond point O and point P lies on the solidus and represents the saturation limit for N_2O_5 in N_2O_4 at $+15^\circ C$. A similar intersection of the liquidus and the solidus curves occurs beyond point Q for $-15^\circ C$ with point R in this case illustrating the saturation of N_2O_5 in N_2O_4 at that temperature.

Referring now to Figure 2 of the drawings, apparatus, generally designated 1, for use in a process for producing a solution of N_2O_5 in an organic solvent comprises an electrochemical cell 2 providing respective anode and cathode compartments 10, 20 having a respective anode and cathode (not shown).

The anode compartment 10 forms part of an anolyte loop 11 having an anolyte storage compartment 12 containing $N_2O_5/HNO_3/N_2O_4$. The anode compartment 10 is capable of having a first, anolyte stream of $N_2O_5/HNO_3/N_2O_4$ passed therethrough from the anolyte storage compartment 12 via the anolyte loop 11.

The cathode compartment 20 forms part of a catholyte loop 21 having a catholyte storage compartment 22 containing $N_2O_4/HNO_3/water$. The cathode compartment 20 is capable of having a second, catholyte stream of $N_2O_4/HNO_3/water$ passed therethrough from the catholyte compartment 22 via the catholyte loop 21.

An explanation of the functioning of such electrochemical cells can be found in UK Patent No. 2 245 003. Essentially, a first, anolyte stream of $N_2O_5/HNO_3/N_2O_4$ is passed through the anode compartment 10, and a second, catholyte stream of $water/HNO_3/N_2O_4$ passed through the cathode compartment 20 whilst applying a potential difference between the anode and the cathode.

In this way electrical current is passed through the cell 2 and N_2O_5 electrochemically formed in the anode compartment 10.

It is envisaged that, in use, the catholyte loop 21, would initially contain concentrated (typically 98%) HNO_3 but would build up a considerable concentration of water and N_2O_4 during the electrolysis. During operation of the process small quantities of the catholyte stream would be removed in a continuous manner and the catholyte stream replenished with fresh HNO_3 . The material removed would be treated to remove water as dilute HNO_3 residual substantially water-free HNO_3 and N_2O_4 being recycled.

The anolyte loop 11 contains the anolyte, which would initially be N_2O_4 in HNO_3 but would build up to a steady state (under extraction conditions) containing at least 15% and 20% respectively of N_2O_5 and N_2O_4 (by weight), during electrolysis depending on the temperature of the anolyte.

It is further envisaged that the electrochemical cell 2 would employ a cationic exchange membrane such as NAFION 324 or NAFION 350 which are proprietary materials manufactured by Messrs DuPont de Nemours. In the present process, the concentration of N_2O_4 in the anolyte is greater than 20% w/w so that a cation exchange membrane can be used without incurring an unacceptably low efficiency.

The apparatus further provides means by which a minor portion (say between 1% and 20%) of the $N_2O_5/HNO_3/N_2O_4$ anolyte stream can be divided off from the rest of the anolyte stream: the divided portion is shown as 31 on Figure 1. By dividing off only a small proportion of the anolyte for further treatment, the main electrochemical process can be operated in a continuous manner under constant steady state conditions and

Date: 17 FEB 1998

solute/solvent equilibrium can be maintained throughout. Moreover, by using a continuous separation process it is only necessary to remove a relatively small proportion of the solute, N_2O_5 , and since phase separation into N_2O_4 and HNO_3 phases occurs under essentially equilibrium conditions elaborate countercurrent methods involving mass transfer of solute are not required. It will be appreciated then that the application of the continuous process of separation to the continuous output from the electrolytic process provides a highly economical procedure overall and one which is well suited to an industrial process.

The apparatus also provides a mixer 32 to which the minor portion is passed, and in which further N_2O_4 may be introduced into the minor portion. Thereafter the minor portion (with or without added N_2O_4) may be cooled to a temperature of around $-5^\circ C$ to $+15^\circ C$ using the cooler 33.

The apparatus also provides a separator 34 to which the (optionally cooled) solution or mixture is then passed. The separator 34 allows the minor portion to separate into two parts, namely an upper N_2O_4 layer containing N_2O_5 and small amounts of HNO_3 and a lower HNO_3 layer containing both N_2O_5 and N_2O_4 .

The separator 34 may additionally include cooling means whereby the minor portion may be maintained at the desired temperature so as to promote the formation of the upper and lower layers and take off means by which the upper and lower layers may be made remote from one another.

There is further provided abstracting means, in this embodiment, in the form of a crystalliser 41 to which the upper N_2O_4 layer is passed. In the crystalliser 41 the N_2O_4 layer is chilled to induce N_2O_5 precipitation. Because at lower temperatures the viscosity of the

Date 17 FEB 1998

mixture becomes too high to allow satisfactory separation of the crystalline N_2O_5 from the liquor, a temperature of -15°C represents a practicable lower limit for operation of crystalliser 41.

The N_2O_5 crystals obtained from the crystalliser are only slightly contaminated with HNO_3 and N_2O_4 and can thence be removed and redissolved in a suitable organic solvent, such as dichloromethane.

The HNO_3 solvent phase produced by the separator 34 is recycled by return to the anolyte loop 11.

Further, effluent N_2O_4 remaining after abstraction of N_2O_5 from the N_2O_4 layer is recycled by feeding to an N_2O_4 storage tank 42, from which tank 42 the divided portion 31 may be injected with N_2O_4 in the mixer 32 in an amount sufficient to saturate the portion prior to separation thereof in the separator 34, as previously explained.

Such recycling of what would otherwise be classed as waste streams obviates the need to dispose of such, and provides an associated cost advantage.

The particular advantage of the process described herewith may be said to depend on the fact that the HNO_3 phase has a high temperature solubility coefficient with respect to N_2O_4 but a lower coefficient with respect to N_2O_5 which permits a rapid separation of the liquid phases without crystallization of solid N_2O_5 when there is a small reduction in temperature of the mixture and that the N_2O_4 phase has both a low content and low coefficient of solubility of HNO_3 but a high coefficient in respect of N_2O_5 thus permitting the rapid and easy formation of relatively pure N_2O_5 crystals on reducing the temperature of this phase. Hence a two stage reduction in temperature with an intermediate phase separation stage will effect transfer of the N_2O_5 from a saturated single

phase three component mixture into a solution in N_2O_4 from which it is readily crystallizable in an essentially pure form which is suitable for re-solution in a suitable organic solvent.

Operation of the process of this present invention may now be exemplified in the following manner.

Example 1

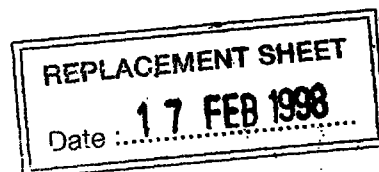
Based on a process of operating an electrochemical cell to generate N_2O_5 in a mixture of N_2O_4 and HNO_3 in accordance with known procedures (see UK Patent No. 2 245 003), synthetic mixtures of all three components were prepared and mixed thoroughly before being each allowed to separate into two layers which were then isolated. The synthetic mixtures each replicated a product of such an electrochemical cell to which N_2O_4 had been added and which had been cooled to a temperature of $15^\circ C$. After separation, samples of each layer were analysed to provide the composition of the upper and lower phases. The results are given in Table 2.

TABLE 2

%w/w in mixture N_2O_4 N_2O_5 HNO_3			%w/w in upper layer N_2O_4 N_2O_5 HNO_3			%w/w in lower layer N_2O_4 N_2O_5 HNO_3		
47	19	34	75	17	8	36	20	44
46	22	32	71	20	9	30	23	47

Example 2

A synthetic mixture with a composition corresponding approximately to that of the upper layers obtained in Example 1 was prepared gravimetrically. The mixture was then chilled to yield crystals which were filtered off and washed with cold dichloromethane. Analyses of the



original synthetic mixture and of the crystalline product obtained before and after washing are given in Table 3.

TABLE 3

%w/w original mixture N ₂ O ₄ N ₂ O ₅ HNO ₃			%w/w wet crystals N ₂ O ₄ N ₂ O ₅ HNO ₃			%w/w washed crystals N ₂ O ₄ N ₂ O ₅ HNO ₃		
68	28	4	8	87	5	0	100	0

The processes described in Examples 1 and 2 and in relation to the process flow diagram of Figure 2 may now be further explained with reference to Figure 3 which shows a simplified representation of the phase diagram of Figure 1 with the solidi and liquidi of that diagram only drawn in. In addition, the phase diagram of Figure 3 shows certain tie lines which connect the compositions of two liquid phases co-existing in equilibrium. Such liquid phases in equilibrium are possible where the respective compositions at a given temperature each lie on one of the two liquidi for that temperature.

For example, data points A and L on the left hand axis of the diagram of Figure 1 represent two compositions which are in equilibrium and which are connected by a tie line lying along the left hand axis. Moving to compositions further to the right on each liquidus, those pairs of compositions which are in equilibrium will be indicated by tie lines which lie broadly parallel to the left hand axis, their exact disposition reflecting the preferential uptake of the solute N₂O₅ in one of the solvent phases.

Point V represents a typical anolyte composition for operation of an electrochemical cell at +15°C, ie with ca. 30 wt% N₂O₄ and ca. 23 wt% N₂O₅. Injection into this composition of N₂O₄ (with efficient mixing) is represented by movement in the direction of the arrow along the line VV', the composition V' corresponding to the composition

of the mother liquor which remains after ultimate crystallisation of N_2O_5 . Dependent on the respective quantities of added N_2O_4 and of the minor portion of the anolyte of composition V, the mixture may be said to reach a composition represented on the diagram of Figure 3 by point W. This, in the embodiment chosen, represents a composition with circa. 46 wt% N_2O_4 and circa. 19 wt% N_2O_5 , that is, of roughly the same composition as the mixtures of Example 1.

Composition W is not a stable mixture and on being allowed to divide will form two phases or layers with compositions represented by respective points W' and W" lying on the two liquidi at either end of the tie line W'W". From this point the two layers are separated and the heavier acid layer represented by point W' is returned back to the anolyte loop (as previously described in connection with Figure 2), while the composition W", in which N_2O_4 is the solvent, is fed to the chiller and crystalliser. The compositions at W' and W" correspond approximately to those of the two layers produced in Example 1 (Table 2).

When the N_2O_4 solvent layer (W") is cooled, solid pure N_2O_5 crystallises out as indicated by line W'X'. As N_2O_5 crystallises out (ie a composition represented by X'), the remaining N_2O_4 layer becomes enriched with respect to N_2O_4 as represented by a composition at point X. This composition is again unstable and the result could be a further separation to compositions represented by points Y and Y' (shown this time as lying at either end of tie line YY' on the respective liquidi at -15°C , because of the cooling of the liquid). In practice any separate HNO_3 which may arise (ie. composition Y) will be entrained in the major N_2O_4 phase (composition Y') and will be returned to the earlier part of the process via the N_2O_4 storage tank 42 (Figure 2).

Date: 17 FEB 1998

In summary, for a given anolyte composition V, the quantity of N_2O_5 extracted is controlled by the flow rate of the anolyte loop take-off, by the quantity of N_2O_4 liquor mixed with it, and by the relative temperatures of the separation stage and the crystalliser.

Date 17 FEB 1998

CLAIMS

1. A process for producing a solution of N_2O_5 in an organic solvent comprising the steps of:

passing anolyte and catholyte streams of N_2O_4 in HNO_3 through respective anode and cathode compartments of an electrochemical cell whilst applying a potential difference between an anode and a cathode thereof, whereby electrical current is passed through the cell and N_2O_5 is electrochemically formed in the anode compartment, characterised by the further steps of:

dividing off a portion of the anolyte stream and, by either or both steps of cooling or addition thereto of N_2O_4 with thorough mixing, causing the divided portion to separate to produce a first N_2O_4 solvent phase containing N_2O_5 and a second HNO_3 solvent phase also containing N_2O_5 ;

separating the two phases in a separator; and

recovering N_2O_5 from the first N_2O_4 phase into an organic solvent to produce a solution of N_2O_5 therein;

and wherein the concentration of N_2O_4 in the anolyte stream is maintained at at least 20 weight%.

2. A process according to claim 1, wherein after addition of N_2O_4 to the divided portion, the portion is cooled to a temperature of between -5 and $+15^\circ\text{C}$.

3. A process according to claim 1 or claim 2, wherein the concentration of N_2O_4 in the anolyte stream is maintained at at least 30 wt%.

4. A process according to any of claims 1 to 3, wherein the concentration of N_2O_5 in the anolyte stream is maintained at at least 15 wt%.



* C L M S *

Date **17 FEB 1998**

5. A process according to claim 4, wherein the concentration is maintained at at least 20 wt%.
6. A process according to any one of the preceding claims, wherein the temperature of the anolyte stream exiting from the electrochemical cell is maintained in the range of 0 to 30°C.
7. A process according to any one of the preceding claims, wherein the portion of the anolyte stream which is divided off is a minor portion thereof.
8. A process according to claim 7, wherein the minor portion comprises from 1 to 20 wt% of the anolyte stream.
9. A process according to claim 8, wherein the minor portion comprises approximately 5 wt% of the anolyte stream.
10. A process according to any one of the preceding claims, wherein the N_2O_5 product is recovered from the first N_2O_4 phase by chilling the N_2O_4 phase to induce crystallization either in bulk or on a cold surface and then respectively filtering off the solid or draining the liquid phase from the surface, followed by re-dissolving the solid N_2O_5 in an organic solvent.
11. A process according to any one of claims 1 to 9, wherein the N_2O_5 product is recovered from the first N_2O_4 phase by applying reduced pressure to the N_2O_4 phase to cause the solvent N_2O_4 to be distilled off and re-dissolving the N_2O_5 produced in an organic solvent.
12. A process according to any one of claims 1 to 9, wherein the N_2O_5 product is recovered from the first N_2O_4 phase by feeding the N_2O_4 phase directly into an organic solvent and subjecting the mixture to fractional



* C L H S *

Date: 17 FEB 1998

distillation at reduced pressure to remove the volatile N_2O_4 , leaving a solution of N_2O_5 in the organic solvent.

13. A process according to any one of the preceding claims, wherein the organic solvent is dichloromethane or acetonitrile.

14. Apparatus for use in a process for producing a solution of N_2O_5 in an organic solvent, which apparatus comprises:

an electrochemical cell providing respective anode and cathode compartments having a respective anode and cathode, the compartments being capable of having respective first, anolyte and second, catholyte, streams of N_2O_4 in HNO_3 passed therethrough, said cell further having means for applying a potential difference between the anode and the cathode whereby, in use, an electric current passes through the cell and N_2O_5 is formed electrochemically in the anode compartment, characterised in that the apparatus further comprises:

means for dividing off a portion of the anolyte stream and means for cooling the divided portion to produce a first N_2O_4 solvent phase containing N_2O_5 and a second HNO_3 solvent phase;

a separator for separating the two phases; and

means for recovering N_2O_5 from the first N_2O_4 phase into an organic solvent to produce a solution of N_2O_5 therein.

15. Apparatus according to claim 14, further comprising means for injecting a stream of N_2O_4 into the divided off portion of the anolyte stream prior to cooling the portion.



Date 17 FEB 1998

16. Apparatus according to claim 14 or 15, wherein effluent N_2O_4 remaining after recovery of N_2O_5 from the N_2O_4 phase is recycled to the anolyte stream of the electrochemical cell.
17. Apparatus according to claim 16, wherein at least a part of the effluent N_2O_4 is recycled to be injected into the divided portion of the anolyte stream.
18. Apparatus according to any of claims 14 to 17, wherein the separated HNO_3 solvent phase is returned to the anolyte stream of the electrochemical cell.
19. A process for producing a solution of N_2O_5 in an organic solvent as hereinbefore described with reference to Figs 1 to 3.
20. An apparatus for use in a process for producing a solution of N_2O_5 in an organic solvent as hereinbefore described with reference to Fig 2.

