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ABSTRACT

A number of amine resins with an excess of amine groups have been prepared and studied for their absorption and desorption of CO_2 in the gas phase. Evaluations were made of types of amines, cycled life in absorption and desorption, and the effect of swelling agents including H_2O on the efficiency of these amine resins. It was found that a swelling agent was necessary for measurable absorption to take place, with water-swelled resins showing more absorption than nonaqueous-swelled resins. A water-swelled amine resin cycled 1008 times through the absorption and desorption of CO_2 from air containing 1-1/2 percent CO_2 showed no decrease in absorption efficiency on a volume basis, but there was a noticeable loss of amine resin during this operation. The loss of H_2O during reactivation of the resin may cause an engineering problem which cannot be satisfactorily overcome in the practical application of these resins for CO_2 removal in submarines.

PROBLEM STATUS

This is a preliminary report on this phase of the problem. Work has been suspended on this phase for evaluation of other methods on the project.

AUTHORIZATION

NRL Problem C08-05
Project NS 131-004

Manuscript submitted August 29, 1957

REMOVAL OF CO₂ FROM SUBMARINE ATMOSPHERES BY AMINE RESINS

A FEASIBILITY STUDY

INTRODUCTION

Purpose

This report covers work done on an interrupted basis during 1953-1955 as part of a long-range program at NRL in the field of submarine air purification. The purpose of this phase was to investigate a new class of solid, heat-regenerative CO₂ absorbents which had been suggested in the course of earlier work on selectively permeable membranes. Because work has been suspended on this method of air purification, this report was written to summarize the completed work (a) to permit consideration of the idea by others who may succeed in reaching more optimistic conclusions and (b) to avoid duplication of effort elsewhere.

Background

Criteria for selecting CO₂ removal processes for submarines include power, volume, weight, toxicity, and simplicity, with the relative importance assigned to each dependent on the type of ship, tactical concepts, and policy. In general, there are two main types of processes, regenerative and nonregenerative, and in the particular case of nuclear powered submarines only the regenerative type appears suitable, since volume requirements for nonregenerative systems such as lithium hydroxide become prohibitive for long dives. The above criteria also apply in comparing regenerative systems among themselves, and in the period during which this work was done power was considered much more important than it is today. For this reason research emphasis was on finding systems offering the possibility of power reductions over the existing ethanolamine scrubbers with volume being considered important but secondary. These scrubbers use solutions containing 70-80 percent water which are boiled under pressure during regeneration and cooled to near room temperature for absorption. Although the latent heat of vaporization and specific heat losses are reduced by the use of heat exchangers and sometimes by vapor compression, they are still significant due to the high concentration of water. On this basis the concept of using a solid in granular or sheet form seemed attractive. Figure 1 is a schematic of a typical ethanolamine scrubber such as is in use today on the USS NAUTILUS (SSN571), and from this it can be seen that the most obvious sources of heat loss are the condenser and the cooler. Another point of interest in a solid system is its possible lack of vapor pressure, which would eliminate the need of the air purifier used to prevent odor and toxic effects.

The work which actually led to development of the present thermally regenerative solids was concerned with finding a membrane which is readily permeable to CO₂ but impermeable to N₂ and O₂. The apparatus used to measure membrane permeabilities is shown schematically in Fig. 2. By valve manipulations the desired gas (CO₂, O₂, N₂) can be placed on one side of the membrane and a hard vacuum maintained on the other. The mercury slug (F) shows the amount of gas permeating under these conditions. This technique was original at NRL but has since appeared in the literature (1) as the result of

NOTE: W. E. McConaughy, General Dynamics Corporation, Electric Boat Division, Groton, Connecticut

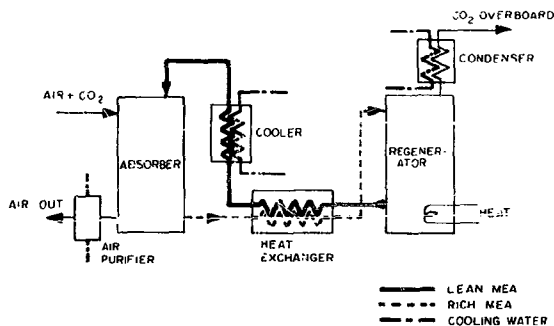


Fig. 1 - A typical ethanolamine scrubber

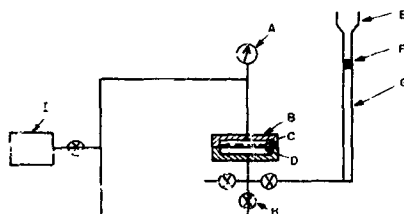


Fig. 2 - Apparatus to measure membrane permeabilities: A - vacuum gage; B - frame to hold test membranes; C - coarse screen backing for test membranes; D - test membrane; E - mercury trap; F - mercury drop; G - calibrated glass capillary tube; H - Hoke valve; I - vacuum pump

independent work. The NRL results have never been reported, but even natural rubber which was found to have the highest CO_2 permeability showed little promise for submarine use. A sheet only 0.001 inch thick requires around 11,000 square feet of surface per pound of CO_2 per hour, which is considered excessive. Loss of N_2 and O_2 and probable large vacuum pump requirements are also undesirable.

In the course of the above work several types of membranes were prepared at NRL in an effort to increase the CO_2 solubility and hence the permeability. (Permeability is a function of the product of solubility and diffusivity.) Figure 3 illustrates results obtained which, while logical, were not anticipated. Teflon is representative of previously tried materials which show a steady-state condition. The NRL resin, however, shows a

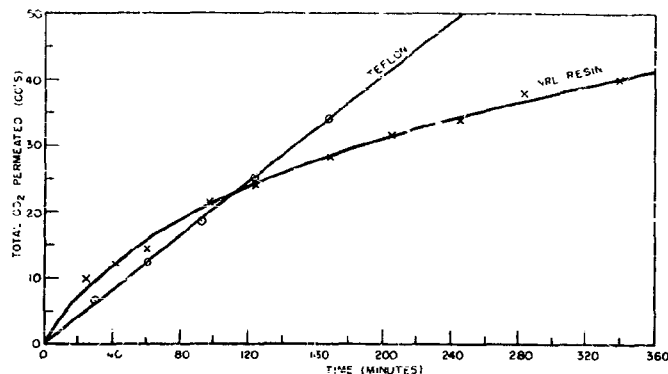


Fig. 3 - CO₂ permeability of Teflon and of an NRL resin

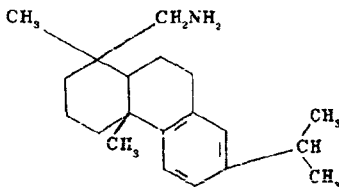
decreasing permeation rate indicating failure to desorb on the evacuated side. Since this resin was made by adding catalytic quantities of polyamines to a commercial epoxide resin, it appeared that reactive amine groups were present which held the CO₂ too tightly for vacuum release at room temperature. This suggested the possibility of using these amine groups as the basis of a heat-regenerative CO₂ absorbent.

To exploit this possibility resins then were made with the intent of linking a large number of reactive amine groups to an insoluble resin matrix, in contrast to the conventional procedure of using only small quantities for curing purposes. Because such resins could not be made directly in sheet form and because for experimental purposes membranes are more difficult to contact with a gas stream and regenerate by heating, subsequent work was done with granular materials.

Now, amine polymers can be either liquids or solids, and for submarine use neither form has unquestioned superiority. Theoretically the liquid would be best because it can be used easily in a continuous process, is easy to heat, conserves power by the use of heat exchangers, and can be used in conventional gas absorption equipment. In general, however, liquid polymers have two serious drawbacks--they are viscous and they are subject to continuing polymerization producing solid insoluble products. For this reason work at NRL was confined to the solid form ("amine resins"), although several liquid polymers were made but not evaluated.

There are a great number of chemical ways in which reactive amine groups can be linked to a matrix to form a solid insoluble resin. For example, a proposal submitted to the Bureau of Ships in 1954 by Atlantic Research Co. suggested 20 possible syntheses. Initially, however, a brief survey was made to determine whether any commercial resinous materials were available which were known to absorb CO₂ and regenerate by heating. Two such materials were found and examined, although both were liquids. The first was

Rosin Amine D produced by the Hercules Powder Co. This viscous, high boiling (187°C - 211°C at 5 mm Hg) liquid is a rosin derivative believed to be composed mainly of dehydroabietylamine,



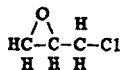
The second material obtained was polyamide resin No. 100 produced by the General Mills Co. by the condensation of dimerized linoleic acid with dimethylenetriamine. Preliminary measurements at 1.5 percent CO_2 for both of these materials in the form of impregnated filter paper or vermiculite showed their absorption rates to be too low to be of interest.

The NRL resin had a much higher rate and capacity in the same preliminary measurements and this was of interest for further study. Synthesis of other types of solid amine resins was not undertaken during the course of subsequent work because (a) the NRL resin was felt to be sufficiently representative to permit evaluation of the idea and (b) synthesis of this resin was quick and easy with various polyamines. Of incidental interest was the fact that the structure was similar to ethanolamine monomers used in industrial gas scrubbers (Girbotol Process), i.e., both are hydroxyl amines containing hydroxyl and amine groups on adjacent carbons.

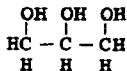
PREPARATION OF RESINS

Characteristics of NRL Resins

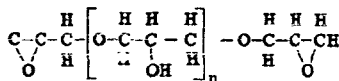
Preparations of amine resins by Mr. S. B. Crecelius* at NRL were made in the same general way, that is by adding a polyamine to Epon 862, a commercial epoxide resin. This epoxide resin is one of a series of compounds sold by Shell Chemical Corp. but, unlike others in the series, contains no aromatic groups. It could be the condensation product of epichlorohydrin



and glycerine

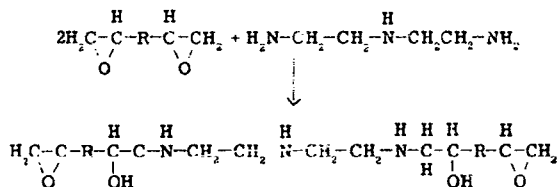


and has the following general structure:

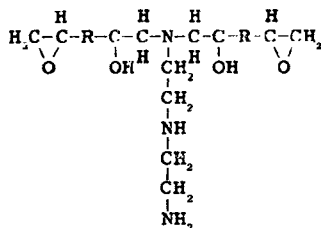


*Now at Economic Laboratory Incorporated, St. Paul, Minn.

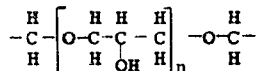
As mentioned earlier it is conventional to add small amounts (3-5 percent) of aliphatic polyamines to this liquid to make hard, durable coatings and cements. Few, if any, reactive amine groups are left in this case, and the intent is to obtain good physical properties and chemical inertness. As synthesized at NRL, however, much larger amounts of the same and other types of amines were added to obtain maximum reactivity with CO_2 . In addition, a volatile solvent such as xylene was used with the intent of producing porosity when it was evaporated. The following is an example of the type of reactions occurring during synthesis:



or



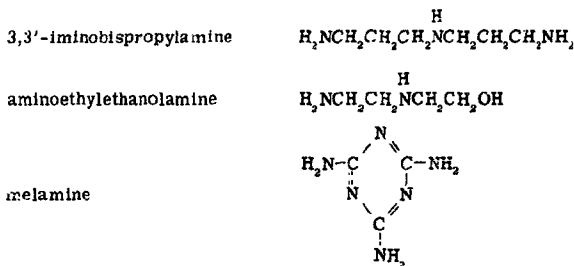
where R is



From this it can be seen that chains of various lengths can be built containing primary, secondary, and tertiary amine groups and that crosslinking is produced also. However, as in ion exchange work (2), the product cannot be accurately characterized or exactly reproduced.

In the preceding example, diethylenetriamine is used for illustration, but other polyamines were also used. The following is a list of those tried:

ethylenediamine	$\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$
diethylenetriamine	$\begin{array}{c} \text{H} \\ \\ \text{H}_2\text{NCH}_2\text{CH}_2\text{NCH}_2\text{CH}_2\text{NH}_2 \end{array}$
tetraethylenepentamine	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \\ \quad \quad \\ \text{H}_2\text{NCH}_2\text{CH}_2\text{NCH}_2\text{CH}_2\text{NCH}_2\text{CH}_2\text{NCH}_2\text{CH}_2\text{NH}_2 \end{array}$



The one exception to this general method of synthesizing the resins occurred when the reactants were tetraethylenepentamine and epichlorohydrin. However, this would be expected to give the same type of resin as a product.

For evaluation the resins were ground in a Wiley mill to 20 mesh while swollen, and then sieved and washed in various ways which are described later. The final products were granules having varying degrees of hardness and susceptibility to swelling with water and organic liquids.

Procedure

Table 1 gives the compositions of the resins studied. The following synthesis procedure for resin of batch 2 is representative of all but two in this list. The ingredients were mixed with xylene in a flask equipped with a stirrer without external heating. The reaction was exothermic and the temperature gradually rose to 80°C. After about 40 minutes of stirring the reaction mixture set to a resinous gel which was removed from the flask and broken into small pieces. The material then was ground on a Wiley mill using a 20-mesh screen and evacuated overnight to remove the bulk of the solvent.

The two exceptions to this general procedure were batch No. 5 in which melamine was reacted directly with Epon 562 with no xylene present and batch No. 21 for which neither Epon 562 nor xylene were used. In both cases it is felt that the product was of the same type as the others in the series.

Various methods of preparing the resins for evaluation were used initially, but for most of the work reported here the resins were steamed in tubes to remove CO₂ and the remaining xylene prior to use.

RESIN EVALUATION

Although both absorption rate and capacity are important characteristics for CO₂ absorbents, it was felt that rate is the controlling factor for submarine applications. For this reason, the various forms of NRL amine resins were screened on the basis of absorption rate under conditions similar to those of a submarine, i.e., 1.5 percent CO₂, 70°F, and around 70 percent R.H. From these rate studies in which the effects of composition, water content, and gas flow rate were determined a single resin was selected for equilibrium (capacity) studies. Also, several side studies were carried out including cyclic life, swelling produced by nonaqueous liquids, and the effect of various preliminary washing agents. For comparative purposes several commercial anion exchange resins were examined. Details of these studies follow.

TABLE 1
Compositions of NRL Amine Resins

Batch No.	Amine	Composition			
		Amine Weight		Epon 562 Weight	
		Grams	Mols	Grams	Epoxide Equivalent
1	Tetraethylenepentamine (TEP)	70	0.37	140	1
2	Diethylenetriamine (DET)	103	1	140	1
3	TEP	100	0.53	140	1
4	Ethylenediamine	80	0.78	140	1
5	Melamine	126	1	140	1
6	DET	206	2	280	2
7	TEP	189	1	140	1
9	DET	206	2	280	2
10	3,3'-iminobispropylamine	131	1	140	1
11	DET	206	2	280	2
12	Aramoethylethanolamine	104	1	140	1
13	Aminoguanidine bicarbonate	136	1	140	1
15	TEP	280	1.48	560	4
16	DET	414	4	560	4
21	Made up of 203 parts TEP, 207 parts epichlorohydrin, and 500 parts water by weight				

Rate Studies

Apparatus - Figure 4 is a schematic of the apparatus used for absorption rate measurements. The glass sample tube (E) was 2.5 cm in diameter and was filled to a height of 15 cm, giving a sample volume of 75 cc. The entire apparatus was located in a constant-temperature room maintained at 70°F, and the 1.5 percent CO₂ test gas was humidified to around 70 percent R.H. by immersing the saturator (C) in a 59°F water bath. This method of humidification was used for all runs except one series in which the saturator was pressurized at room temperature so that the humidity of the gas stream at atmospheric pressure could be varied easily by changing the saturator pressure. The flowmeter (B) was used only as a flow indicator to avoid errors from varying back pressures and true flow were obtained from the wet test gas meter (I). The drying tube (F) was a precaution against errors from water vapor and drops going through the infrared CO₂ analyzer (G).

Procedure and Results - The general procedure was to water-wash and steam the resin after grinding and to pack the sample tube to a height of 15 cm by light tapping. Gas flow rates varied but were adjusted to produce early breakthrough (detectable quantity of CO₂ in the effluent) so that the apparent absorption rate was not limited by the amount of CO₂ available. Excessive flow rates were avoided because as the effluent CO₂ concentration

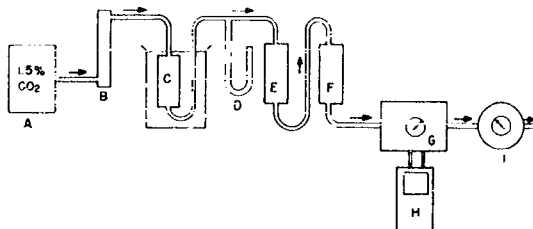


Fig. 4 - Amine resin absorption rate apparatus: A - supply tank; B - flowmeter; C - saturator tube filled with water-soaked porous Al_2O_3 beads in a constant-temperature water bath; D - water manometer; E - absorption tube; F - drying tube filled with Drierite; G - Liston-Becker infrared CO_2 analyzer (Model II); H - Esterline-Angus recorder; I - wet test gas meter

approached the influent concentration, calculation errors became large. Absorption rates were calculated per unit of resin volume on an 1-hour basis using flow rates and integrated time-efficiency curves (inlet and outlet CO_2 concentrations vs time).

Effect of Type Amine Added - Table 2 summarizes the absorption rates obtained for a number of different amine resin types. Although one additional type (3,3'-iminobispropylamine + Epon 562) was made, it was not evaluated because of poor physical properties. In some cases several batches of a given formulation were made and gave different absorption rate figures, and in these cases representative runs were selected for Table 2. Comments on physical properties are in terms of ease of filling sample tubes and passing an air stream through the resin under the test conditions.

TABLE 2
 CO_2 Absorption Rate Versus Composition of Resin

Batch No.	Preparation	Absorption (mg CO_2 /cc resin/hr)	Physical Characteristics
4	Ethylenediamine + Epon 562	12.9	very poor
5	Melamine + Epon 562	0.0	very good
9	DST + Epon 562	20.6	good
15	TEP + Epon 562	7.3	good
12	Aminoethylethanolamine + Epon 562	9.3	good
13	Aminoguanidine bicarbonate + Epon 562	0	good
21	TEP + Epichlorohydrin + H_2O	6.0	very good

Effect of Amine Content - The effect of varying the amount of polyamine was studied for one type of amine resin (TEP + Epon 562). The results from absorption rate measurements, Karl Fischer moisture measurements, and visual examination are listed in Table 3.

Effect of Washing Agent - The resins after being ground contained residual xylene and unidentified viscous liquids. Table 4 compares absorption rates and physical characteristics for material from one batch of one type resin (DET + Epon 562) that was unwashed, washed with methyl-ethyl ketone (MEK), and washed with water.

TABLE 3
CO₂ Absorption Rate Versus Amount TEP Used in Resin Preparation

Batch No.	Mols. TEP Epoxide Equivalent	Absorption (mg CO ₂ /cc resin/hr)	Physical Characteristics
1	0.37	6.9	Tough, rubbery; swelled a bit in water
3	0.53	8.7	Not quite as tough; swelled; 83 percent water
7	1.0	27.7	Very soft and rubbery; 84 percent water

TABLE 4
Effect of Washing Agent on CO₂ Absorption Rate (DET + Epon 562)

Wash	Absorption (mg CO ₂ /cc resin/hr)	Physical Characteristics
No wash	36.7	Rubbery, tended to stick together and clog test tube, tended to set on heating
Methyl-ethyl ketone	36.0	No significant stickiness or thermosetting
Water	20.6	No significant stickiness or thermosetting

Effect of Water Content - Resins which were good absorbents showed considerable swelling with water. Therefore the type showing the best absorption rate in Table 2 (DET + Epon 562) was investigated for the effects of ambient relative humidity and water content. Samples of the same batch were placed in containers having constant, known relative humidities and allowed to reach equilibrium. The results are plotted in Fig. 5 as resin water content vs relative humidity. Figure 6 shows the absorption rates of the samples as a function of water content, with rate being calculated in terms of dry and wet weights as well as volume.

Effect of Gas Flow Rate - A series of runs were made to verify the assumption that the flow rate should be adjusted to give early breakthrough. Figure 7 shows the time-efficiency curves at different flow rates for one batch of one type resin (DET + Epon 562). Calculated absorption rates and final absorption efficiencies (percent of inlet CO₂ being removed at the end of one hour) are given in Table 5.

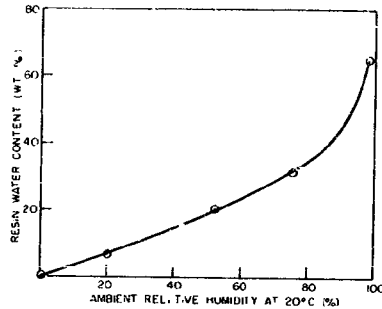


Fig. 5 - Water content vs relative humidity.
Resin: DET + Epon 562, less than 30 mesh
when dry.

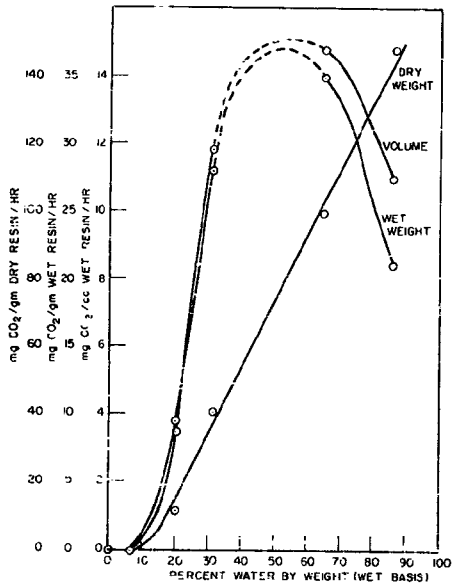


Fig. 6 - Absorption rate vs water content.
Resin: DET + Epon 562, less than 30 mesh
when dry.

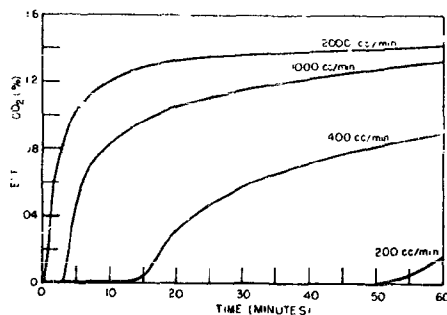


Fig. 7 - Absorption efficiency vs time at various flow rates. Resin: DET + Epon 562.

TABLE 5
CO₂ Absorption Rate of TEP + Epon 562 Versus
Gas Flow Rate

Flow Rate (cc/min)	Absorption (mg/cc/hr)	Efficiency After One Hour (percent)
2000	7.2	9
1000	7.3	15
400	6.3	42
200	4.5	89

Commercial Ion Exchange Resins - For comparative purposes representative commercial anion exchange resins were evaluated as to their absorption rate and regeneration at 100°C. Three such resins were selected on the basis of their being representative of weak, medium, and strong base materials. Table 6 lists the results along with those for an NRL resin for comparison.

TABLE 6
Comparative Performance of Anion Exchange Resins

Resin	Type	Absorption Rate (mg CO ₂ /cc resin/hr)	Regeneration (percent)
IR-45*	Weak base	5.4	42
Permutit A†	Medium base	5.6	6
Naicite SAR‡	Strong base	26.9	6
NRL	DET + Epon 562	20.6	100

*From Rohm and Haas Co., Resinous Products Div., Phila., Pa.

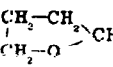
†From Permutit Co., New York, N. Y.

‡From National Aluminate Corp., Chicago, Ill.

10-mm-ID glass tube having a nickel screen near one of the two open ends. The procedure consisted of filling a column 1 inch deep with dry resin (0.05 percent water), adding a considerable excess of swelling agent, and measuring the resin height after the liquid was drained off in one or two days.

Selection of swelling agents was made on the basis of their being high boiling liquids representative of various classes of organic compounds. Low viscosity was considered desirable but not essential. Ketones and aldehydes were not tried, because in general they react with amines. Table 7 lists the various swelling agents tried and shows the volume increase produced by each.

TABLE 7
Amine Resin Swelling Agents

Class	Name	Formula	Ratio of Final Volume to Initial Volume	Final Appearance
-	Water	H_2O	3.0	off-white
Alcohol	n-Octyl alcohol	$CH_3(CH_2)_6CH_2OH$	1.0	yellow
	Benzyl alcohol		4.4	yellow
	Tetrahydrofurfuryl alcohol		3.4	yellow
Polyhydric alcohol	Ethylene glycol	CH_2OHCH_2OH	2.2	yellow
	Glycerine	$CH_2OHCHOHCH_2OH$	2.3	pale yellow
Ether	n-Hexyl ether	$C_6H_{13}OC_6H_{13}$	1.3	yellow
	Diethyl carbitol	$C_2H_5OC_2H_4OC_2H_4OC_2H_5$	1.0	yellow
Ether alcohol	Triethylene glycol	$HOC_2H_4OC_2H_4OC_2H_4OH$	4.1	pale yellow
	Butyl carbitol	$C_4H_9OCH_2CH_2OC_2H_4CH_2OH$	1.2	yellow
Amine	Monoethanolamine	$HOC_2H_4NH_2$	1.6	pale yellow
Amide	Formamide	$HCONH_2$	2.4	pale yellow
Ester	Triacetin	$C_3H_5(CO_2CH_3)_3$	1.2	pale yellow
Hydrocarbon	Dodecane	$CH_3(CH_2)_{10}CH_3$	1.0	yellow

Equilibrium Studies

Apparatus and Method - One batch of the type resin found best in the rate studies (DET + Epon 562) was used in all equilibrium work. The data sought were resin saturations (gm CO_2 /gm resin) as a function of CO_2 partial pressure, and the method used was to confine a known amount of CO_2 over a known amount of resin at the desired pressure and temperature.

Figure 9 shows the apparatus used for the equilibrium measurements. Temperature was controlled and held constant by the indicated water or triethylene glycol bath. Total pressure over the sample (E) was controlled by the mercury leveling bulb and measured by the difference in mercury levels in the gas buret (B) and the manometer (F). By proper manipulation of the 3-way stopcock (A) and knowledge of the free volume of the side-arm (C) and sample bottle (E) it was possible to calculate CO_2 absorption from initial and final readings.

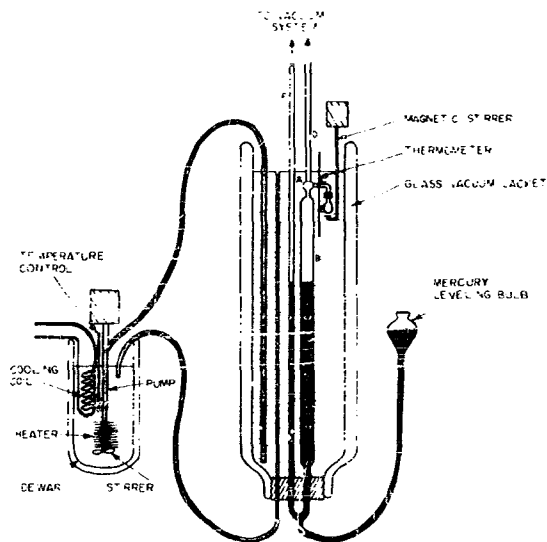


Fig. 9 - Amine resin CO_2 equilibrium apparatus

The above method was adequate for measurements on dry resin, but for resin swelled with water and organic liquids additional measurements and corrections were necessary. In the case of water-swelled resins, the total pressure consisted of the sum of water vapor and CO_2 partial pressures. Therefore a separate determination of the water vapor pressure-temperature relationship for the resin sample was necessary in order to calculate the CO_2 partial pressure for a given total pressure. For the resins swelled with organic liquids such a correction was not required because of the low vapor pressure of

the liquids used. However, since CO_2 solubility is much greater in organic liquids than in water, and since no suitable data were available in the literature separate determinations of this property at various temperatures were made.

Results - The results are given on a weight basis because of the variations in sample tube size and packing density.

Dry Resin - Resin containing less than 0.05 percent residual water showed no significant absorption (<0.4 mg CO_2/gm resin) in 24 hours either at 20°C or 90°C under a CO_2 pressure of 1000 mm Hg.

Water-Swelled Resin - Resin containing 45 $\pm$ 3 percent water was selected for equilibrium measurements from the results of rate vs water content studies. Figure 10 shows the water vapor pressure over this resin as a function of temperature. Free water is also shown for comparison. Figure 11 is a plot of CO_2 equilibrium data for this resin obtained at five different temperatures. Again for comparison water is given also. Since the water vapor pressure of the resin is not affected by CO_2 , a constant value is shown with the temperature for each curve.

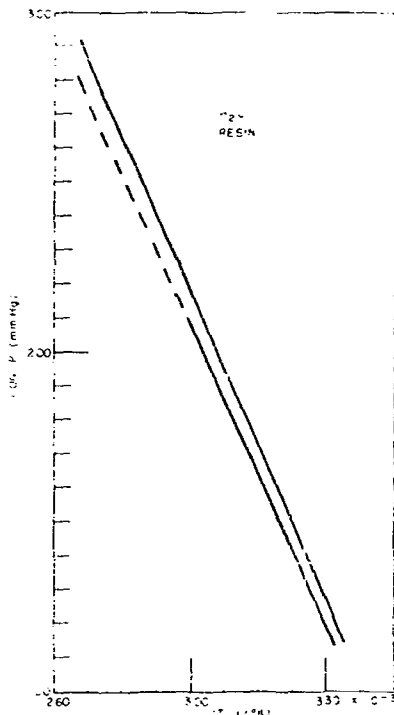


Fig. 10 - Water vapor pressure vs temperature for amine resin containing 45 percent water: (DET + Epon 562)

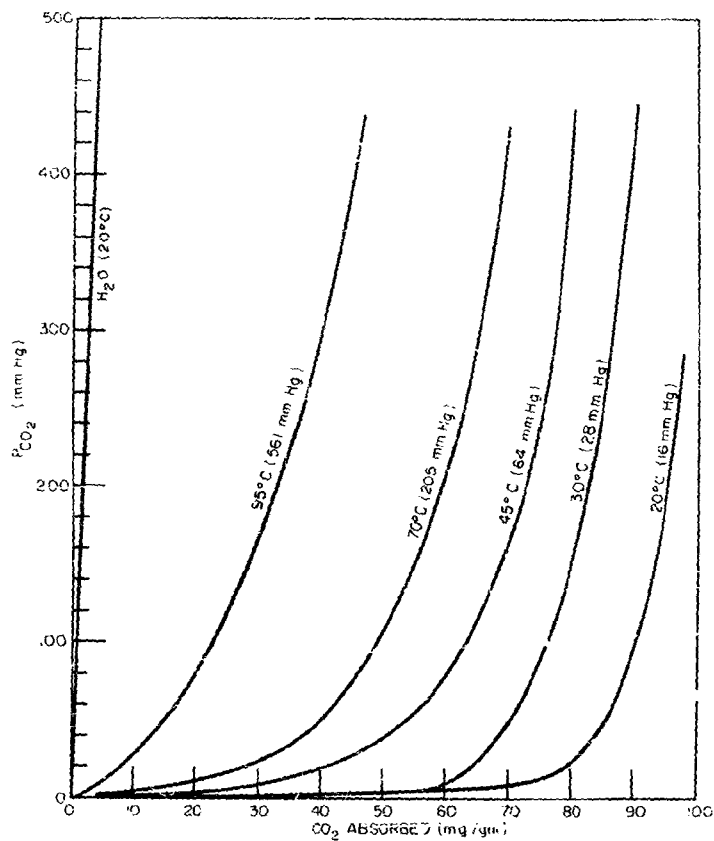


Fig. 11 - CO₂ equilibrium curves for amine resin containing 45 percent water (DET + Epon 562). (Water vapor pressure in equilibrium with amine resin given in parentheses for each temperature plotted.)

Organic-Liquid-Swelled Resins - From the study of swelling agents (Table 7) three liquids were selected for use in equilibrium measurements. Figures 12, 13, and 14 show CO_2 equilibria for formamide, triethylene glycol, benzyl alcohol, and their respective swelled resins at several temperatures. It should be noted that the CO_2 contents of the resins are given in terms of weight of dry resin, so that direct numerical comparisons with the water-swelled-resin curves in Fig. 11 cannot be made. For comparison, however, data for one of the latter type resins are plotted on dry basis in Fig. 14.

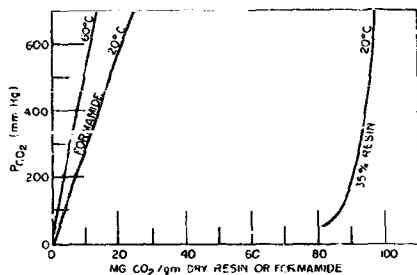


Fig. 12 - CO_2 equilibrium curves for formamide and formamide-swelled resin

Fig. 13 - CO_2 equilibrium curves for triethylene glycol and triethylene-glycol-swelled resin

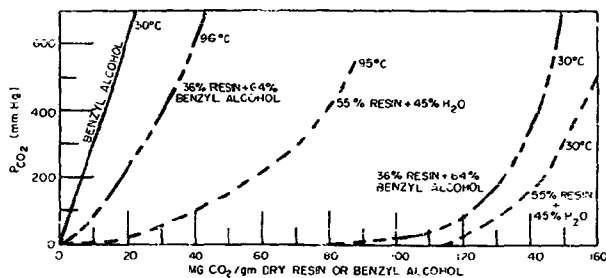
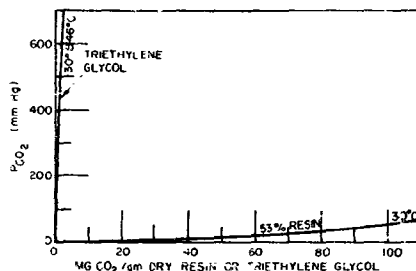


Fig. 14 - CO_2 equilibrium curves for benzyl alcohol, benzyl-alcohol-swelled resin, and water-swelled resin

DISCUSSION

Resin Synthesis

As stated earlier the particular type resin used in this study was selected on the basis of being representative and easily made. It was felt that developing the optimum material was secondary to a determination of the general characteristics and the potentialities of such materials for submarine use. However, a broad synthetic program would be very desirable to obtain the best physical properties and performance, if the basic idea is felt to be of interest. Areas to be studied in such a program include (a) type of reactive amine groups (primary, secondary, or tertiary) producing largest effective capacity, (b) methods of increasing the ratio of amine groups to resin matrix, (c) optimum cross linking to obtain the best compromise between absorption rate and physical properties (hardness, degree of swelling, lack of tackiness, and cold flow), and (d) effect of composition on chemical and thermal stability. An example of (d) is the possibility that tertiary amine groups on a resin matrix will inhibit oxidation of primary groups, analogous to findings for amine solutions (3).

It is generally accepted that for ion exchange resins the exchange rate is a diffusion controlled process, i.e., the chemical reaction is very rapid. Since it is now believed that "amine resins" are really anion exchange resins of a type suitable for thermal regeneration, it is likely that the same diffusional concepts apply. From the standpoint of absorption, therefore, physical form and swelling agent properties, particularly viscosity, are probably of primary importance. For regeneration, however, the character of the reactive amine groups is probably controlling, since this would be expected to affect the CO_2 equilibrium partial pressures and hence the ease of regeneration. Figure 15 illustrates the difference between monomeric primary and secondary amines with the secondary type, diethanolamine, being easier to regenerate. Such a difference is probable for resins also.

Rate Studies

The rate studies represented a restricted effort to obtain the best form of one type of amine resin for further evaluation and to obtain reference data on commercial ion exchange resins. In view of the many difficulties in perfecting techniques for resin preparation and measuring absorption rate it was considered neither feasible nor desirable to study a large number of compositions. Data obtained, while indicative, is not conclusive because of variations between batches of the same resin. Batch variations are normal in resin work, but they were larger with the particular resin used because of the random formation of primary, secondary, and tertiary amine groups as well as linear and crosslinked molecules. Therefore, conclusions based on small differences between single batches are questionable but are valid where a number of repeat batches were made (DET + Epon 562, TEP + Epon 562) or where the rates were much lower (TEP + Epon 532, aminoethylethanolamine + Epon 562, aminoguanidine bicarbonate + Epon 562, melamine + Epon 562). The data in Table 6 for commercial ion exchange resins were taken at the time to indicate the unsuitability of such materials for a temperature regenerative cycle. However, it is now felt that, while this is undoubtedly true of quaternary ammonium compounds such as Nalcite SAR, the weak base resin IR-45 probably showed a poor absorption rate because of its degree of crosslinking. Its incomplete regeneration may have resulted from the formation of more stable urea-type ring compounds. Use of a different polyamine in its synthesis would prevent this.

The resin (DET + Epon 562) which has the highest rate in Table 2 was selected for equilibrium work because it was considered to be the best compromise between performance and physical properties after being effectively washed. Table 3 shows a different

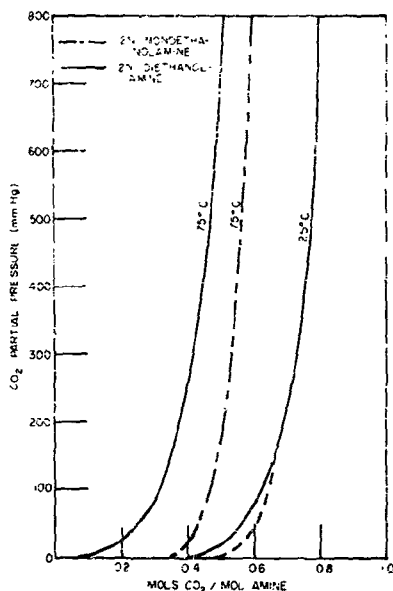


Fig. 15 - CO_2 equilibrium curves for two monomeric amines (from J. W. Mason and B.F. Dodge, Trans. Am. Inst. Chem. Engrs. 32:27, 1936)

resin having a higher rate but unsatisfactory physical properties. Table 4 shows a much higher absorption rate for the same resin when water soluble materials are not washed out. It is not known what these materials are since methyl-ethyl ketone (MEK) is a solvent for both of the ingredients, DEI and Epon 562. Evaporation of the wash water leaves a clear viscous liquid which may be of interest as a CO_2 absorbent itself.

The effect of water content on the resin absorption rate (Fig. 10) appears to have a logical explanation. As stated above the absorption rate is probably a diffusion controlled process. Since the diffusion of gases is more rapid through liquids than through solids, increasing the amount of water would be expected to increase the rate, if the main resistance is in the granules as suggested in Ref. 4. A possible explanation for the shape of the volume and wet weight curves is that initially the addition of water increases the pore size with a resultant increase in gas phase diffusion. Eventually the pores would fill with water, necessitating more of the slower liquid phase diffusion. The zero rate in the dry condition may be due to the fact that the carbamate formation necessitated in the absence of water does not occur at such low CO_2 partial pressures. However, later equilibrium studies with resin swelled with nonaqueous liquids indicates that while the rate may be very low the reaction does occur.

Cyclic Life

Cyclic life studies were made on a resin having improved physical properties at the expense of absorption performance. However, results are still applicable to related resins and show that there is no significant chemical degradation in 2016 hours running on a steam regenerated cycle. The 15 percent loss in total volume may result from a low order of water solubility or from decrepitation. Oxidation stability appears good, since the resin was contacted with air half the time including recurrent periods when it was hot following steaming. Since dry make-up resin could easily be added, resin life appears quite satisfactory.

Swelling Agents

Table 7 shows that the most effective swelling agents were benzyl alcohol, tetrahydrofurfuryl alcohol, triethylene glycol, and water. Examination of this table and Table 8 which lists available physical properties reveals no obvious basis for predicting the effectiveness of organic liquids for this use except for ethers and hydrocarbons. Representatives of these two classes produced no detectable swelling.

TABLE 8
Properties of Resin Swelling Agents

Class	Name	Bp (°C)	Vapor Pressure (mm Hg)		Dielectric Constant	Viscosity at 20°C (cs)	Dipole Moment	Heat of Vap. (cal/gm)	Sp Ht (cal/gm)	Molecular Weight
			20°C	100°C						
	Water	100	17.5	760	81	1.0	1.84	540	1.00	18
Alcohol	n-Octyl alcohol	195			3.4	8.9	1.7	97(196°C)		130
	Benzyl alcohol	205		15	13	5.6		112(204°C)	0.51	108
	Tetrahydrofurfuryl alcohol	176				5.5				102
Polyhydric alcohol	Ethylene glycol	197	0.1	15	41	20	1.7	191(197°C)	0.57	62
	Glycerine	290		0.2	42	1499	1.7	195	0.57	92
Ether	n-Hexyl ether	226	0.07				1.1	69		186
	Diethyl carbitol	189	0.4							162
Ether alcohol	Triethylene glycol	287	0.01	0.35		45			0.60	150
	Butyl carbitol	230	0.02							162
Amine	Monoethanolamine	170	0.4	42		25	1.3	198	0.50	61
Amide	Formamide	211(d)		6	84	3.4			0.55	45
Ester	Triacetin	259				15.1				212
Hydrocarbon	Dodecane	213		12		1.35	0	55	0.52	170

The three nonaqueous liquids selected for equilibrium studies were benzyl alcohol and triethylene glycol on the basis of their swelling effectiveness and formamide on the basis of its low viscosity.

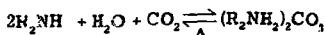
Equilibrium Studies

Results for dry resin confirmed the rate study finding that in the unswelled condition there is no significant amount of reaction between CO_2 and the amine groups present in the resin. Such a reaction should occur analogous to that between an amine and CO_2 to form a carbamate under anhydrous conditions. This has been demonstrated at this Laboratory for diethanolamine under high partial pressures of CO_2 . The reaction in that case is

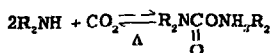


The explanation appears to be physical in nature, since the same resin when swelled with an organic liquid has a definite equilibrium with CO_2 (Figs. 12, 13, and 14) although still under anhydrous conditions. The previously suggested explanation of inadequate pore size may be correct, but it requires that all or nearly all of the amine groups be located in pores and not on the granule surface.

Figure 14 compares equilibria for aqueous and nonaqueous swelled resins at temperatures representative of absorption and regeneration. Water-swelled resin is superior from the absorption standpoint and resin swelled with benzyl alcohol is superior from the regeneration standpoint, i.e., has a higher CO_2 pressure at a given saturation. From an equilibrium standpoint the net capacity in a sublimation cycle would depend primarily on the regeneration conditions. The fact that the nonaqueous curve lies to the left of the aqueous curve at both temperatures can be explained by the fact that tertiary amines cannot form carbamates and thus are not available to combine with CO_2 in the case of the nonaqueous swelled resin. The fact that the relative positions of the curves change with temperatures probably results from the different reactions involved. Thus for an amine in the presence of water the absorption of CO_2 can be illustrated by the following reaction for a secondary amine:



Under anhydrous conditions the reaction would be



A factor of great practical importance is the absorption rate. Although it cannot be seen in Fig. 14, the time to reach equilibrium was much longer for the resin swelled with benzyl alcohol, and to determine the part the swelling agent might play in a diffusional process the following equations from Refs. 5 and 6 was used to calculate comparative liquid diffusivities with CO_2 :

$$D = \frac{B \sqrt{1/M_1 + 1/M_2}}{A_1 A_2 Z_2^{1/2} S^2}$$

where

D - diffusion coefficient (cm^2/sec)

R - universal constant

M - molecular weight

A - abnormality constant

Z - solvent viscosity (cps)

$S = V_1^{1/3} + V_2^{1/3}$ where V is the volume of 1 mol of the gas or liquid at the boiling point.

Table 9 gives comparative results obtained by substituting appropriate figures in this equation. This arrangement in order of decreasing diffusivity agrees with observations made during equilibrium measurements. Water-swelled resins required around one hour to reach equilibrium but resins swelled with triethylene glycol required about a day. While resins swelled with ethylene glycol were not studied, its diffusivity is included for comparative purposes.

TABLE 9
Diffusivities for CO_2 in Resin Swelling Agents

Liquid	Diffusivity (cm^2/sec)	Relative Diffusivity
Water	8.12	1.00
Formamide	3.08	0.38
Benzyl alcohol	1.20	0.15
Ethylene glycol	0.86	0.11
Triethylene glycol	0.37	0.05

Comparison of Figs. 11 and 15 shows that CO_2 equilibria for water-swelled amine resins are of the same type as for aqueous solutions of monomeric amines such as monoethanolamine (MEA) and diethanolamine (DEA). This is not unexpected but could not safely be predicted because of the complex composition and structure of the resins.

Submarine Application

The original interest in amine resins was the possibility of saving power by eliminating water as a major constituent of amine scrubbers. Other interests were elimination of odor and toxicity problems resulting from amine volatility and process simplification by the and toxicity problems resulting from amine volatility and analyses, etc. The concept of elimination of liquid level controls, liquid purges, solution a solid absorbent analogous to lithium hydroxide which can be regenerated by moderate heating and/or evaporation sounded quite attractive—and still does. However, the fact that amine resins do not absorb CO_2 when dry considerably altered the picture on their use, and a later acquired familiarity with aqueous amine solution scrubbers emphasized the power disadvantages of a solid system still containing large amounts of water.

In an effort to better visualize power requirements with various combinations of heat and evacuation, data given in Fig. 11 were used to calculate relative amounts of water and CO_2 removed during regeneration under equilibrium conditions. The results are given in Table 10, where it can be seen that a large amount of water is vaporized even under the best conditions (95°C). Although this compares favorably with a typical MEA scrubber which in at least one Navy design has a regeneration-gas composition of about 3 percent CO_2 and 97 percent H_2O (by volume) at 140°C, this is offset at least partially by the non-recoverable specific heat content of the swelled resin.

TABLE 10
 CO_2 and H_2O Content of Resin Regeneration Gas

Temperature (°C)	Pump-Off Pressure (mm Hg)	Average Composition of Gas Removed *			
		Wt %		Vol %	
		CO_2	H_2O	CO_2	H_2O
95	561	35	65	18	82
70	205	21	79	10	90
45	64	23	77	11	89

*Calculated from Fig. 11 under following assumptions:

1. Each operating cycle removes between 10 and 50 mg CO_2 per gm wet resin.
2. The partial pressure of water remains constant during regeneration.
3. There is no pump-off until the regeneration temperature is reached.
4. The pump-off pressure is water vapor pressure, but gas composition is determined by equilibrium.

Several methods of using amine resins have been considered. In granular form a system analogous to desiccant dehumidifiers (silica gel, activated alumina, etc.) can be visualized using 2 or 3 beds which alternately absorb and regenerate. Under submarine conditions, however, regenerative heating is difficult because a sweep gas cannot be used and heat transfer in a granular bed is very poor when hairpin or surface heaters are used. Although dielectric heating is one way of uniformly heating a solid, it appears unsuitable here because of its power conversion inefficiency, bulk, emission of stray radio-frequency energy, and close electrode spacing.

Infrared heating is another possibility where shallow beds are available. A possible system is to use the resin in a rotary vacuum dryer containing high-temperature infrared sources operating around 2500°K, e.g., tungsten filament lamps. Such a dryer rotates around a horizontal axis, tumbling the granular material to continually contact fresh material with the heated cylindrical sides while a vacuum is applied. In this application, however, the interior might be coated with a good infrared reflector such as gold and heat supplied to the continually changing resin surface by the infrared emitters. If the dryer were of evacuated double wall construction and the interior walls had minimum mass, equipment heat losses should be small. Absorption could be carried on advantageously in

the same equipment. Once a stream of air could be passed axially through the dryer while it was rotating, thus providing good contact between gas stream and resin at very little pressure drop. A possible power advantage of such a system is that the CO_2 to H_2O ratio might improve under rate controlling conditions, i.e., CO_2 might desorb faster than water.

Another physical form which has been considered is sheets or membranes. A possible system in this case is a continuous moving sheet similar to a roller towel. High intensity infrared energy could be supplied to both sides of the sheet while passing through the "box" for rapid regeneration, and absorption can occur during the period outside the box. However, using the absorptor rate for the best of the resins studied (DET + Epon 562) and assuming a sheet or belt having a thickness and surface equal to 20 mesh spheres close packed it can be estimated that for 100 men and a 10-minute cycle a belt 3 feet wide by 1500 feet long traveling at 2-1/2 ft/sec is required.

The use of resins swelled with organic liquids appears undesirable for several reasons. First, the absorption rate is quite low, at least with the liquids tried. Second, in spite of their low volatility they introduce potential toxicity problems as in the case of monomeric amine solutions. Finally, due to the nature of the equilibria determined—which are believed to be representative—a low total pressure is required during regeneration to obtain a sufficiently low CO_2 partial pressure. With water systems this is not necessary because the water vapor acts as a sweep.

SUMMARY AND CONCLUSIONS

A solid, temperature regenerative CO_2 absorbent has been studied with regard to its feasibility for submarine air purification. A number of resins synthesized at NRL were used as being representative of a type of anion exchange material designated as amine resins. Variables studied included composition, type and amount of swelling, method of preparation, and test conditions with evaluation being made in terms of absorption rate and equilibria at various temperatures. Consideration of present amine solution scrubbers leads to the conclusion that although amine resins are feasible for submarine CO_2 removal use, they do not appear promising in processes so far visualized. The use of a swelling agent is necessary which in the case of water results in sizeable vaporization power requirements and in the case of nonaqueous liquids introduces toxicity considerations and vacuum requirements.

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