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OFFICE OF THE PROJECT MANAGER CHEM DEMILITARIZATION I--ETC F/6 15/2  
TECHNICAL/ECONOMIC SURVEY OF THE MARKETABILITY OF U.S. ARMY PHO--ETC(U)  
MAY 78 M E HILLMAN, E W HELPER, W GORDON

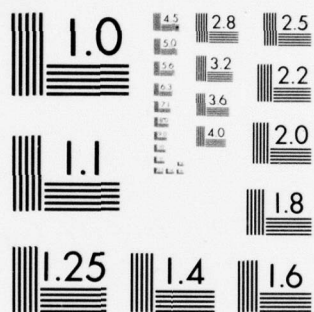
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| 19. KEY WORDS (Continue on reverse side if necessary and identify by block number)<br>Phosgene      Polycarbonates      One-ton cylinders<br>Carbonyl Chloride      Monoisocyanates      106A500X containers<br>Diisocyanates      Pesticides<br>TDT      Pharmaceuticals<br>MDI      Gas distributors                                                                                                                                                                                                                                                                                                                    |                                                                          |                                             |
| 20. ABSTRACT (Continue on reverse side if necessary and identify by block number)<br>A survey of over 40 industrial companies to determine feasibility and best approach for sale of surplus DOD low-grade phosgene. Fourteen companies expressed an interest in the phosgene and/or associated ton containers. Summary data includes production and capacity of facilities for consumption of phosgene and related end products, quality of phosgene required, and an estimate of suitable marketing approach. Containers included with the phosgene consisted of 106A500X one-ton cylinder and 367 106A500X containers. |                                                                          |                                             |

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FINAL REPORT

on

TECHNICAL/ECONOMIC SURVEY OF  
THE MARKETABILITY OF U.S. ARMY  
PHOSGENE (CARBONYL CHLORIDE)

to

OFFICE OF THE PROJECT MANAGER FOR CHEMICAL  
DEMILITARIZATION AND INSTALLATION RESTORATION  
(OPM CDIR), ABERDEEN PROVING GROUND, MARYLAND

May 17, 1978

by

M.E.D HILLMAN, E. W. HELPER,  
and W. GORDON

BATTELLE  
Columbus Division  
505 King Avenue  
Columbus, Ohio 43201

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### EXECUTIVE SUMMARY

The cost of buying, installing and operating the necessary equipment to redistill approximately 2 million pounds of surplus Army phosgene would probably be prohibitive. Most industrial contacts who would comment on this topic indicated that the cost of redistillation would probably greatly exceed the cost of decontamination (neutralization). This indicates that surplus Army phosgene should be used for those reactions that do not require high purity phosgene. Some products that can be made with low grade phosgene are:

- Carbonates
- Chloroformates
- Chlorothioformates
- Carbamoyl chlorides
- Pesticides

Materials that require high purity (>99 percent) phosgene in their manufacture are:

- Diisocyanates (TDI, MDI, etc.)
- Polycarbonates
- Peroxycarbonates
- Pharmaceuticals

Manufacturers of these latter materials generally have no interest in low-grade surplus Army phosgene.

During the course of this investigation, BCD identified 14 companies that have some interest in purchasing surplus Army phosgene. These companies are identified in the Battelle report. All of these companies would like to be notified by the Army of any future bidding announcements. One strategy that might be employed to expedite the removal of the phosgene from RMA, is to make the phosgene available to any company on basically the same contractual basis as the successful Arapahoe bid. The Army could then select the "winning bidder or bidders" according to the most acceptable removal schedule.

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INTRODUCTION

Phosgene was originally purchased by the Army as a chemical warfare agent. In the early 1960's, this chemical was declared obsolete. About 5.7 million pounds of phosgene was sold from Rocky Mountain Arsenal (RMA) to two purchasers before shipments were suspended in 1969. On March 30, 1976 legislation PL 94-251 permitted disposition of the remaining phosgene by sales. Approximately 1.8 to 2.0 million pounds of phosgene with containers is available for sale.

Because OPM CDIR does not have the available necessary in-house capability to perform the tasks required, Battelle was requested to do this project.

Objectives

The overall objective of this study is to collect and analyze data about the potential marketability of Army phosgene. The information obtained will be used to determine the best approach for the sale of the existing Army inventory of low-grade phosgene.



To provide the Army with the information necessary to determine the feasibility and best approach for sale of the existing Army inventory of low-grade phosgene, the following data was collected.

(1) Production/capacity

- U.S. manufacturers
  - production and/or capacities
  - quantities for sale versus captive use
- End products
  - quantities used for each

(2) Quality

- Determine quality required for each end product/process
- Outline purification schemes for each quality level required
- Evaluation of the feasibility of direct use of the low-grade phosgene in the various uses

(3) Marketability

- Make preliminary estimates of the most suitable marketing approach based on:
  - sale on an FOB-origin versus destination basis
  - purification (if needed) at RMA versus contractors site.

Scope

The scope of this project includes the possible sale in the United States of approximately 1.8 million pounds of phosgene. The study also includes the possible sale of the following one ton storage and shipping containers (DOT 106A500X).

| Storage containers      | Shipping containers (with gas tight bonnet) |
|-------------------------|---------------------------------------------|
| 850 full at RMA         | 307 full at RMA                             |
| <u>368</u> empty at RMA | 12 empty at RMA                             |
| Total 1218              | <u>48</u> full at Arapahoe Chemicals        |
|                         | Total 367                                   |

### PRINCIPAL FINDINGS

Over 80 contacts were made to knowledgeable individuals at 40 industrial companies. Fourteen companies (Table 1) expressed an interest in either the phosgene, the cylinders or both. Several of these companies are very eager to obtain the surplus Army phosgene and/or cylinders as soon as possible. A list of all companies contacted is included in Appendix A.

#### Companies Contacted

The companies contacted were manufacturing companies that produced one or more of the following products.

| <u>Product</u>                       | <u>Percentage of U.S.<br/>Phosgene utilized</u> |
|--------------------------------------|-------------------------------------------------|
| ● Phosgene                           | -                                               |
| ● Diisocyanates (TDT & MDI)          | 89                                              |
| ● Polycarbonates                     | } 5                                             |
| ● Monoisocyanates                    |                                                 |
| ● Other chemical intermediates       |                                                 |
| ● Pesticides                         |                                                 |
| ● Pharmaceuticals                    |                                                 |
| ● Gas manufacturers and distributors | 6                                               |

#### Phosgene Manufacturers

Because the 1.8 million pounds of surplus Army phosgene represents only about 1/10 of one percent of the U.S. annual phosgene capacity, the large manufacturers cannot efficiently use such small amounts. Also in 17 of the 19 U.S. phosgene plants the production is essentially limited to captive use. For these reasons phosgene manufacturers had little interest in either the phosgene or the cylinders.



TABLE 1. COMPANIES INTERESTED IN SURPLUS ARMY PHOSGENE  
AND/OR CYLINDERS

| Company                      | Degree of Interest |           |
|------------------------------|--------------------|-----------|
|                              | Phosgene           | Cylinders |
| Consolidated Chemical        | H                  | H         |
| Chemical Commodities         | H                  | H         |
| Jones Chemical               | M                  | H         |
| Union Carbide-Linde Division | L                  | H         |
| Manley-Regan                 | N                  | H         |
| Delta Chem                   | L                  | M         |
| BASF-Wyandotte               | M                  | N         |
| Rubicon                      | M                  | N         |
| Minerec                      | M                  | N         |
| Olin                         | M                  | N         |
| Matheson Gas Products        | M                  | N         |
| Chemetron                    | L                  | L         |
| Union Carbide                | L                  | N         |
| Eastman Kodak                | L                  | N         |

Key: H = High interest

M = moderate interest

L = low interest

N = no interest

Source: Battelle contacts with industry

### Diisocyanate Manufacturers

Toluene diisocyanate (TDI) and methylenebis (4-phenyl isocyanate) (MDI) manufacturers require phosgene of very high purity (99 to 99.9 percent) since the final products, TDI and MDI are not purified and any impurities would end up in the product. The cost of purifying 1.8 million pounds of phosgene would be prohibitive according to some contacts and would probably cost more than disposal/decontamination costs.

### Polycarbonate (PC) Manufacturers

PC manufacturers have no interest in surplus Army phosgene for the same reasons as the diisocyanate manufacturers.

### Monoisocyanate Manufacturers

Since most monoisocyanates are volatile and a final purification (distillation) is normally carried out, impure phosgene can be utilized since impurities can be removed at this final purification stage.

### Other Chemical Derivative and Intermediate Manufacturers

Other chemical derivatives and intermediates such as carbonates, chloroformates, chlorothioformates and carbamoylchlorides are also volatile and can be purified by distillation. Companies that produce these derivatives could probably also use surplus Army phosgene without purification except for filtration. Peroxycarbonates require high purity phosgene because of their propensity to decompose, sometimes violently.

### Pesticide Manufacturers

Not all companies that produce phosgene derived pesticides handle phosgene itself since many pesticides can be made from previously mentioned intermediates such as monoisocyanates, chloroformates, chlorothioformates and carbamoyl chlorides. Impurities, such as iron salts, that would arise from using impure phosgene for pesticide manufacture would probably not be a major problem.

### Pharmaceutical Manufacturers

All contacts made with companies that produce pharmaceuticals were adamant about not using impure phosgene. The FDA would probably not allow it. The major bad actor is the free chlorine. The  $\text{Cl}_2$  could result in chlorinating organic molecules and could result in toxic and/or carcinogenic impurities in the final product. Also carbon tetrachloride ( $\text{CCl}_4$ ) is carcinogenic and would have to be removed completely before the drug could be formulated and sold. For these reasons possible applications in the pharmaceutical industry were not pursued in depth.

### Gas Manufacturers and Distributors

Some of the larger gas manufacturers and distributors were contacted to determine if they had interest in either the gas cylinders or the phosgene. Several of these companies expressed definite interest in cylinders or phosgene or both. These companies are included in Table 1.

### Quality of Phosgene Required

The quality of phosgene required for each end product application is indicated in Table 2. It should be noted that the polymer, peroxide and pharmaceutical applications require very high purity phosgene and should not be considered further as possible outlets for

surplus impure Army phosgene. It should be noted that equipment for purifying surplus Army phosgene to meet the requirements of these applications would probably require one to two years to purchase and install. Also the capital costs would probably exceed the corresponding costs for decontamination. For these reasons Battelle suggests that other areas that do not require such high purity phosgene be pursued by the Army. These applications are indicated in Table 2 as areas requiring only about 95 percent phosgene purity.

#### Purification Schemes

Essentially all industrial contacts indicated that prior filtration of the phosgene would be very desirable. This was particularly true with those contacts that have had previous experience with the RMA phosgene. Several of the latter reported that there was "gummy polymeric material" in the phosgene that resulted in blocking feed lines and equipment. One contact said the "first dozen or so" cylinders received from the Army were good but the rest were bad. A good filtration prior to delivery would greatly expedite disposition of this material.

Alternatively, the Army could do a simple vapor transfer of the phosgene from a full cylinder to a clean empty cylinder. This could be done by connecting the two cylinders together then warming up the full cylinder and cooling the empty cylinder. The phosgene would vaporize then recondense in the empty cylinder. This should remove all solids and high boiling contaminants. However, it would not remove the chlorine (the worst contaminant according to most contacts) unless a precut were taken and discarded (decontaminated). The boiling points of phosgene and chlorine are +7.6 and -34.05, respectively. Since chlorine is considerably more volatile than phosgene, it will tend to vaporize first. If the first one or two percent of the vapors were decontaminated most of the chlorine would probably be removed.



TABLE 2. QUALITY REQUIRED FOR PHOSGENE APPLICATIONS

| Phosgene Derivatives | Required Purity | Significant Contaminants           | Purification Required |
|----------------------|-----------------|------------------------------------|-----------------------|
| TDI/MDI              | > 99%           | Cl <sub>2</sub> , Fe               | Redistillation        |
| Polycarbonates       | > 99            | Cl <sub>2</sub> , Fe               | Redistillation        |
| Monisocyanates       | ~ 95            | --                                 | Filtration            |
| Carbonates           | ~ 95            | --                                 | Filtration            |
| Chloroformates       | ~ 95            | --                                 | Filtration            |
| Chlorothioformates   | ~ 95            | --                                 | Filtration            |
| Carbamoyl chlorides  | ~ 95            | --                                 | Filtration            |
| Peroxy carbonates    | > 99            | Fe, Cl <sub>2</sub>                | Redistillation        |
| Pesticides           | ~ 95            | --                                 | Filtration            |
| Pharmaceuticals      | > 99            | Cl <sub>2</sub> , CCl <sub>4</sub> | Redistillation        |



The cost of redistillation of the phosgene to meet the requirements of polymer, peroxide or pharmaceutical applications would probably not be justified. All correspondents who would comment on this point indicated that the cost of distillation would probably exceed the cost of decontamination. One phosgene manufacturer said that when a below specification batch was produced, it was decontaminated (destroyed). (Note that this comment was made by a representative of a company with existing distillation equipment.) A second contact with this manufacturer indicated that the main reason for discarding bad batches of phosgene was due to plugging of lines when carbon monoxide was added to consume excess chlorine.

In summary the Army might agree to filter the phosgene in the process of transferring it into the shipping containers, if this is practical. It is probably not necessary for the Army to purify the phosgene further. Sufficient markets exist for filtered surplus Army phosgene so that the markets requiring high purity phosgene need not be considered.

#### Marketability

The potential marketability of surplus Army phosgene appears high enough, at least initially, to consider only an FOB origin basis. Of course, the Army should cooperate in any reasonable way to expedite the transfer, loading and transport of material.

Purification of the phosgene (other than filtration as mentioned previously) by redistillation at RMA should probably not be considered because of the exceedingly high cost. Purification by redistillation, if needed, should primarily be considered at the contractors site at his expense.

A strategy that might be used to expedite the removal of the phosgene from RMA, would be to make the phosgene available to any company on basically the same contractual basis as that contained in the successful

Arapahoe bid. That is the price of the phosgene and cylinders could be the same as the accepted Arapahoe bid, but the Army would be able to select the successful bidder(s) based on his or their removal schedule and cylinder return schedule. It is anticipated that the most acceptable removal schedule would approximate 25 one ton cylinders per week based strictly on the Army's filling capability. Actually the optimum removal schedule is somewhat higher than 25 per week.

Since we understand the Army can fill 25 cylinders per week, the 850 full storage containers could be transferred into shipping containers in 34 weeks. There are also 307 full shipping containers at RMA or a total of 1157 full containers. If all of the containers were removed in 34 weeks, the average removal rate would be 34 containers per week. This, of course, assumes that emptied shipping containers would be returned starting in the second or third week and on a continuing basis thereafter. Thus the optimum removal rate would be 34 containers per week. The Army could accept the bidder that could most closely meet this schedule. It might be necessary to sell phosgene to more than one company, however, this would probably not be as desirable as having a single contractor.

### RESEARCH RESULTS

An initial literature search was made to determine the U.S. companies that may have an interest in either the phosgene or the containers. These manufacturing companies were organized according to the following product classifications:

- Phosgene
- Diisocyanates (TDI, MDI)
- Polycarbonates
- Monoisocyanates
- Other chemical intermediates produced from phosgene
- Pesticides produced from phosgene
- Miscellaneous pharmaceuticals that can utilize phosgene
- Gas manufacturers and distributors.

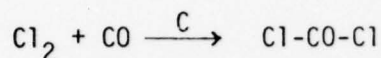
Each of the above classes of companies will be discussed briefly in the following sections of the report.

#### Manufacturers of Phosgene

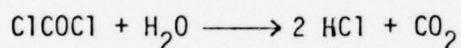
There are presently 17 U.S. manufacturers of phosgene and 19 plants. These plants and their capacities are listed in Table 3. Phosgene plant capacities range from about 5 million pounds to about 300 million pounds. Of the 17 manufacturers of phosgene there are only two (Chemetron and Van De Mark) that are well recognized merchant marketers of phosgene. The other 15 companies (17 plants) produce phosgene for captive use. Almost half of the plants (9) are in the Gulf states (Texas, Louisiana, and Alabama), and the rest are east of the Mississippi River. None of these plants is close to RMA.

Chemistry

Phosgene is prepared by passing a mixture of equivalent (molar) amounts of chlorine and carbon monoxide over an activated carbon catalyst bed.



An excess of carbon monoxide is usually used so as to consume completely all of the chlorine. The catalyst bed must be cooled externally, because the reaction is very exothermic. Most of the carbon monoxide available for phosgene manufacture in the United States is produced from natural gas. Trace amounts of untreated methane ( $\text{CH}_4$ ) in the carbon monoxide are chlorinated to produce carbon tetrachloride ( $\text{CCl}_4$ ) as a trace impurity in the phosgene. Traces of moisture in the Army phosgene should have reacted completely with the phosgene according to the equation:



This is an irreversible reaction which should have been complete years ago, so the analytical documents that indicate that water is present in the Army phosgene are probably erroneous.

Manufacturers of Diisocyanates (TDI, MDI)

There are ten U.S. manufacturers of TDI (toluene diisocyanate). Seven of the ten TDI producers have phosgene plants that are designed to supply exactly the amount of phosgene required by their TDI plants. Table 1 lists the phosgene capacity and also the phosgene capacity required for TDI, MDI, and polycarbonate plants. When these two numbers are equal, the remainder column in Table 3 is zero. This occurs for 10 of the 19 phosgene plants. That is, 10 of the U.S. phosgene plants are devoted entirely to TDI, MDI, and polycarbonate manufacturing (no surplus phosgene is produced).

It should be noted that 66 percent of U.S. phosgene capacity is specifically dedicated to TDI manufacture and 23 percent to MDI. This leaves only about 11 percent for all other applications.



| Company                          | Location             | Capacity | Phosgene Requirements for: (a) |             | Other        |
|----------------------------------|----------------------|----------|--------------------------------|-------------|--------------|
|                                  |                      |          | TDI                            | MDI         |              |
| Allied                           | Moundsville, WV      | 100      | 100                            |             | 0            |
| BASF Wyandotte                   | Geismar, LA          | 130      | 130                            |             | 9            |
| Rubicon (Unifroyal + ICI)        | Geismar, LA          | 125      | 55                             | 70          | 0            |
| Chemetron*                       | LaPorte, TX          | 67       |                                |             | 67           |
| Dow                              | Freeport, TX         | 130      | 130                            |             | 0            |
| DuPont                           | Deepwater, NJ        | 135      | 135                            |             | 0            |
| PMC (b)                          | Baltimore, MD        | (6) (u)  |                                |             | (6)          |
| GE                               | Mount Vernon, IN     | 60       |                                | 60 (Lexan®) | 0            |
| Jefferson (Texaco) (c)           | Port Neches, TX      | (30) (c) |                                | (30) (c)    | 0            |
| Minerac                          | Baltimore, MD        | 8        |                                |             | 8            |
| Mobay                            | New Martinsville, WV | 250      | 130                            | 99          | 17 (Merlon®) |
| Mobay                            | Baytown, TX          | 250      | 235                            |             | 15 (Merlon®) |
| Olin                             | Ashtabula, OH        | 50       | 50                             |             | 0            |
| Olin                             | Lake Charles, LA     | 120      | 120                            |             | 0            |
| PPG                              | Barberton, OH        | 5        |                                |             | 5            |
| Stauffer                         | Cold Creek, AL       | 25       |                                |             | 25           |
| Story (d)                        | Muskegon, MI         | (10) (d) |                                |             | (10) (d)     |
| Union Carbide                    | Institute, WV        | 140      | 72                             |             | 68           |
| Upjohn                           | LaPorte, TX          | 300      |                                | 225         | 75           |
| Van De Mark*                     | Lockport, NY         | 8        |                                |             | 8            |
| TOTAL                            |                      | 1738     | 1157                           | 394         | 92           |
| Percent                          |                      | 100      | 66                             | 23          | 5            |
| Phosgene required/lb. of product |                      | 1        | 1.3                            | 0.9         | 0.42         |

\* Merchant Marketer

(a) These numbers are the approximate amount of phosgene required for each use based on published figures and/or industrial contacts.

(b). FMC stopped producing phosgene and chloroformates in 1974

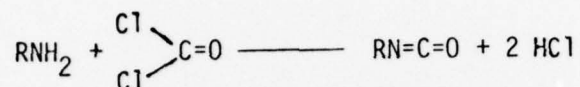
(c) Jefferson is no longer producing phosgene or MDI.

(a) Company filed for bankruptcy in 1976. Cordova, the buyer of the plant and technology, is not manufacturing isocyanates and does not plan to do so before 1980.

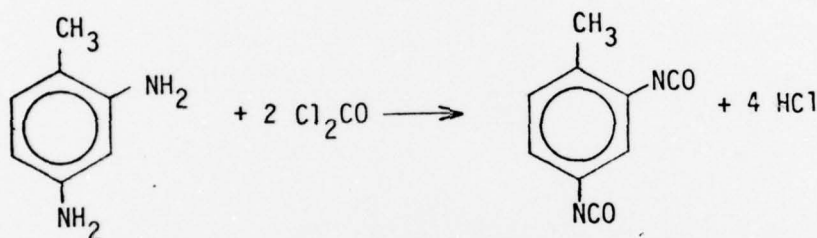
Source: Battelle estimates and calculations.

Chemistry

Isocyanates are made by reacting phosgene with a primary amine ( $\text{RNH}_2$ ):

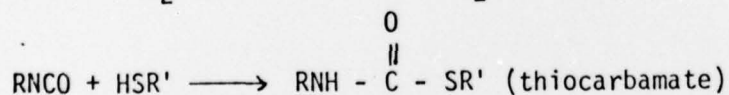
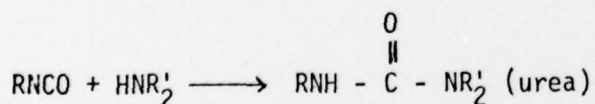
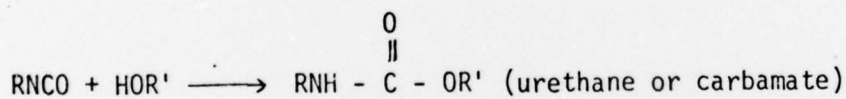


TDI is made from an aromatic diamine according to the equation:



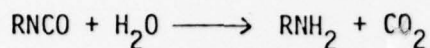
The structure of MDI is:  $\text{OCN} - \text{C}_6\text{H}_4 - \text{CH}_2 - \text{C}_6\text{H}_4 - \text{NCO}$

Reactions of Isocyanates. Isocyanates are very reactive. Some examples are:



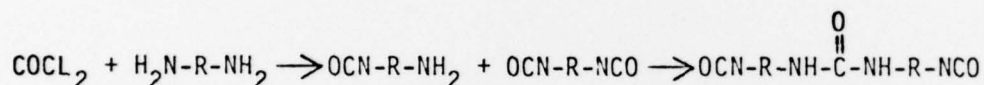
When a diisocyanate such as TDI is reacted with a dihydroxy compound (glycol), both ends of both molecules can react, and high molecular weight polymers (plastics) are produced.

If a controlled amount of water is incorporated in the system, the following reaction also occurs:



The  $\text{CO}_2$  is a gas and causes the polymerizing mixture to foam as it solidifies. This is the way polyurethane foam cushions for furniture and automobiles are made.

It should be noted that, when diisocyanates are made from diamines, the isocyanate groups can react with amine groups before all of these have been converted to isocyanate groups by the phosgene. For this reason the product actually obtained is an oligomer containing several TDI or MDI precursor molecules bonded together by urea linkages.



Since the molecule is not a single chemical entity, it cannot be purified by the conventional means of crystallization or distillation. For this reason, the phosgene used to produce diisocyanates must be very pure, and the Army surplus phosgene would not be suitable without extensive and very expensive purification prior to use.

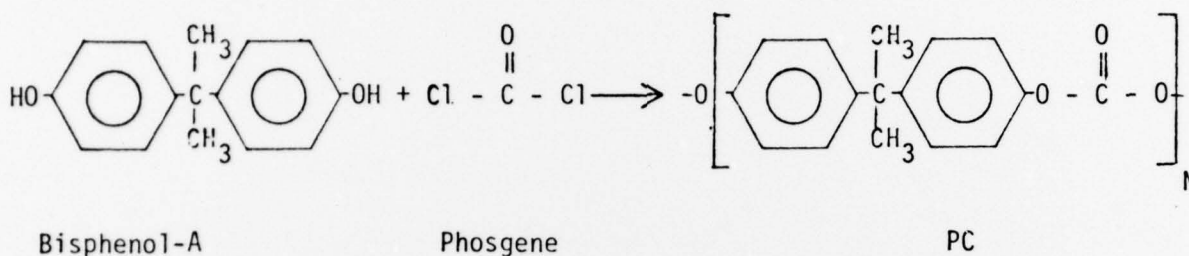
#### Manufacturers of Polycarbonates

Two U.S. companies (GE and Mobay) manufacture polycarbonates (PC) in three plants (see Table 3). The capacity for the manufacture of PC requires an annual capacity of 92 million pounds of phosgene or about 5 percent of total U.S. phosgene capacity.

GE's entire 60 million pound capacity for phosgene is used in the manufacture of PC (Lexan<sup>®</sup>). Mobay uses about 32 million pounds of phosgene per year for polycarbonates. Mobay's total phosgene capacity is about 500 million pounds per year. In addition to PC, Mobay makes TDI, MDI, and 7 miscellaneous isocyanates.

Chemistry

Polycarbonates are made by reacting a diol (glycol) directly with phosgene. The only diol of important commercial significance is bisphenol-A. The equation is:



PC is a clear, colorless, tough plastic that competes with polymethylmethacrylate (PMMA) and specially treated glass in the shatter-resistant glazing industry.

Like TDI and MDI, PC is prepared directly from phosgene with no significant purification of the final polymer. PC, therefore, requires a very high purity phosgene in its manufacture. Surplus Army phosgene without extensive purification (redistillation) would not be suitable for PC manufacture.

Manufacturers of Monoisocyanates

Companies that manufacture monoisocyanates from captive phosgene are indicated in Table 3. Companies that produce isocyanates from either purchased or captive phosgene are listed in Table 4. Companies that use purchased phosgene to prepare monoisocyanates are naturally likely prospects for purchasing surplus Army phosgene.

Chemistry

The basic chemistry of isocyanates is outlined briefly in earlier sections on Chemistry under Manufacture of Diisocyanates and Reactions of Isocyanates.



An important fact is that the monoisocyanates are usually low molecular weight chemical species and consequently can be purified by distillation. Thus, impurities in surplus Army phosgene will usually be removed from monoisocyanates during the conventional purification techniques. For this reason, manufacturers of monoisocyanates could probably use surplus Army phosgene without prior distillation. Solid particulate matter could block lines, plug valves and gum up equipment, so filtration is probably desirable.

Manufacturers of Other Chemical Derivatives and  
Intermediates Produced from Phosgene

Table 4 also lists companies that produce other chemical intermediates produced from phosgene. Some of these intermediates are:

- Carbonates
- Peroxycarbonates
- Chloroformates
- Chlorothioformates
- Carbamoyl chlorides.

Chemistry

The following equations indicate how the above intermediates could be produced from phosgene.

TABLE 4. U.S. PRODUCERS OF MERCHANT PHOSGENE -  
DERIVED CHEMICAL INTERMEDIATES

| Parent Company     | Division or Subsidiary    | Plant Location       | Derivative                                                                                                                              |
|--------------------|---------------------------|----------------------|-----------------------------------------------------------------------------------------------------------------------------------------|
| Akzona             | Armak Process Chemical    | Bayport, TX          | Di (sec-butyl) peroxydicarbonate<br>Di (2-ethylhexyl) peroxydicarbonate<br>Di (-n-propyl) peroxydicarbonate<br>Isopropyl percarbonate   |
| Chemetron          | Chemical Products         | LaPorte, TX          | 15 chloroformates<br>Diethyl carbonate<br>Dimethyl carbonate<br>Dipropyl carbonate                                                      |
| Eastman Kodak      | Eastman Organic Chemicals | Rochester, NY        | p-Nitrophenyl isocyanate<br>p-Tolyl isocyanate<br>Diphenyl carbamoyl chloride<br>Phenyl chloroformate                                   |
| Jakem Industries   |                           | New Haven, CT        | >100 aromatic isocyanates                                                                                                               |
| Minerac            |                           |                      | Diethyl carbonate<br>Dimethyl carbonate<br>Ethyl chloroformate<br>Isobutyl chloroformate<br>Methyl chloroformate                        |
| Mobay Chemical (a) | Industrial Chemicals      | New Martinsville, WV | m-Chlorophenyl isocyanate<br>p-Chlorophenyl isocyanate<br>3,4-Dichlorophenyl isocyanate<br>Phenyl isocyanate<br>Ethyl chlorothioformate |

| Parent Company | Division or Subsidiary | Plant Location | Derivative                                                                                                                                                                                                                         |
|----------------|------------------------|----------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Pennwalt       | Lucidol                | Buffalo, NY    | Dicetyl peroxydicarbonate<br>Dicyclohexyl peroxydicarbonate                                                                                                                                                                        |
|                |                        |                | tert-Butyl peroxyisopropyl carbonate<br>Di (sec-butyl) peroxydicarbonate<br>Di (n-propyl) peroxydicarbonate                                                                                                                        |
|                |                        | Genesee, NY    |                                                                                                                                                                                                                                    |
| PPG            | Industrial Chemicals   | Barberton, OH  | Allyl diglycol carbonate<br>tert-Butyl peroxyisopropyl carbonate<br>Di (sec-butyl) peroxydicarbonate<br>Di (2-ethyl hexyl) peroxydicarbonate<br>Di-n-propyl peroxydicarbonate<br>Isopropyl chloroformate<br>Isopropyl percarbonate |
|                |                        |                |                                                                                                                                                                                                                                    |
|                |                        |                |                                                                                                                                                                                                                                    |
| R.S.A.         |                        | Ardsley, NY    | Benzl chloroformate<br>2-Chloroethyl carbonate<br>2-Chloroethyl chloroformate<br>Phenyl carbonate<br>Tetra isoamylammonium thiocyanate                                                                                             |
|                |                        |                |                                                                                                                                                                                                                                    |
|                |                        |                |                                                                                                                                                                                                                                    |
| Stauffer       |                        | Cold Creek, AL | n-Propyl chlorothioformate                                                                                                                                                                                                         |

| Parent Company                | Division or Subsidiary | Plant Location                     | Derivative                                                                                                                                                                                  |
|-------------------------------|------------------------|------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Story Chemical <sup>(b)</sup> | Ott                    | Muskegon, MI                       | n-Butyl isocyanate<br>p-Chlorophenyl isocyanate<br>3,4-Dichlorophenyl isocyanate<br>Ethyl isocyanate<br>Isopropyl isocyanate<br>Methyl isocyanate<br>Phenyl isocyanate<br>Propyl isocyanate |
| Union Carbide                 | Chemicals and Plastics | Institute and South Charleston, WV | Methyl isocyanate                                                                                                                                                                           |
| Upjohn                        | Fine Chemical          | North Haven, CT                    | tert-Butyl isocyanate<br><u>p</u> -toluenesulfonyl isocyanate                                                                                                                               |
|                               | Polymer Chemicals      | LaPorte, TX                        | <u>n</u> -Butyl isocyanate<br>tert-Butyl isocyanate<br>Phenyl isocyanate<br>TODI<br>PMPI                                                                                                    |

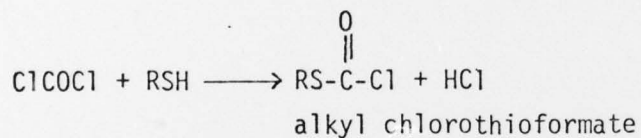
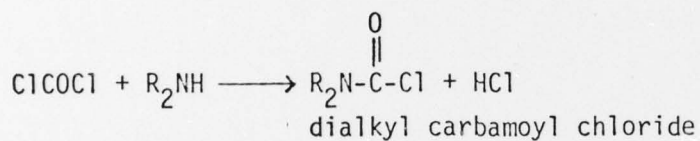
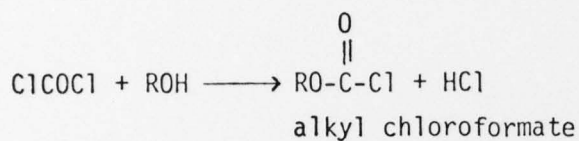
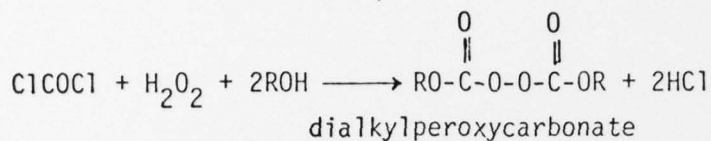
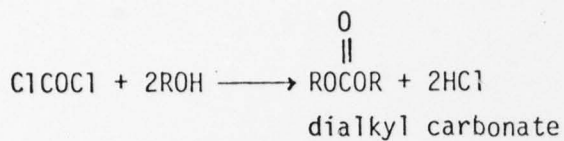
(a) Subsidiary of Bayer AG of West Germany.

(b) Company filed for bankruptcy in 1976. Cordova, the buyer of the plant and technology, is not manufacturing isocyanates and does not plan to do so before 1980.

Sources: (1) Industry contacts.

(2) Stanford Research Institute, 1977 Directory of Chemical Producers, Menlo Park, CA (1977).





#### Manufacturers of Pesticides Produced from Phosgene

Table 5 lists 11 companies that produce 29 pesticides whose basic raw material is phosgene. It should be noted that all of these companies do not necessarily handle phosgene. They might purchase some of the intermediates such as chloroformates or carbamoyl chlorides discussed in the previous section.

#### Chemistry

Phosgene has two reactive chlorines that will react sequentially with active hydrogens attached to heteroatoms (i.e., ROH, R<sub>2</sub>NH, RSH). The nomenclature of the products is indicated in the following tabulation.

TABLE 5. U.S. MANUFACTURERS OF PESTICIDES BASED ON PHOSGENE

| Company                | Plant Location | Pesticide Name (Type) (a)                   | Raw Materials other than Phosgene                          | Capacity, million pounds |
|------------------------|----------------|---------------------------------------------|------------------------------------------------------------|--------------------------|
| Ciba-Geigy             | McIntosh, AL   | Maloran <sup>®</sup> (Chlorobramuron) (H-U) | 3-Cl-4-Br-aniline + O,N-dimethylhydroxylamine              | NA                       |
|                        | Toms River, NJ | Tenor <sup>®</sup> (Chloroxuron) (H-U)      | p-Cl-phenoxyaniline + dimethylamine                        | NA                       |
|                        | McIntosh, AL   | Fluometuron (H-U)                           | m-trifluoromethylaniline + dimethylamine                   | NA                       |
|                        | Palacios, TX   | Diuron (H-U)                                | 3,4-dichloroaniline + dimethylamine                        |                          |
| Colorado International |                |                                             |                                                            |                          |
|                        |                |                                             |                                                            |                          |
| DuPont                 | Belle, WV      | Benonyl <sup>®</sup> (benilate) (F-C)       |                                                            |                          |
|                        | LaPorte, TX    | Diuron (H-U)                                | 3,4-dichloroaniline + dimethylamine                        | (b)                      |
|                        |                | Lorox <sup>®</sup> (linuron) (H-U)          | 3,4-dichloroaniline + O,N-dimethylhydroxylamine            | 30 (b)                   |
|                        |                | Tupersan <sup>®</sup> (sifuron) (H-U)       | aniline + 2 methylcyclohexylamine                          | 30 (b)                   |
|                        |                | Telvar (monuron) (H-U)                      | p-Cl-aniline + dimethylamine                               | 30 (b)                   |
|                        |                | Methomyl (I-C)                              | methylamine + methyl thiomethyl ketone oxime               | 5                        |
| FMC                    | Middletown, NY | oxamyl (Vydate <sup>®</sup> ) (I-C)         | methylamine + 2-oximino-2-thiomethyl-N,N-dimethylacetamide | 11                       |
|                        |                | Furadan <sup>®</sup> Carbofuran (I-C)       | methylamine + 2,3-dihydro-2,2-dimethyl-7-hydroxybenzofuran | 15                       |
|                        |                | Tandex <sup>®</sup> (H-C)                   | dimethylamine + m-aminophenol + t-butyl isocyanate         | NA                       |
|                        | Pittsburgh, PA | Carbyne <sup>®</sup> barban (H-C)           | m-Cl-aniline + 4-Cl-2-butynol-1                            | NA                       |
| El Lilly               | Lafayette, IN  | Spike <sup>®</sup> tebuthiuron (H-U)        | methyl amine + a 1,3,4-thiadiazolamine                     | NA                       |

TABLE 5. (Continued)

| Company       | Plant Location                                      | Pesticide Name (Type) <sup>(a)</sup>                                                                                                                                                                                                                    | Raw Materials other than Phosgene                                                                                                                                                                                                                | Capacity,<br>million<br>pounds   |
|---------------|-----------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------|
| Nor Am Ag.    | Chicago, IL                                         | Carzol <sup>®</sup> (formetanate) (I-C)                                                                                                                                                                                                                 | methyl amine + 3-(dimethylaminomethylene-imino) phenol                                                                                                                                                                                           | 1                                |
|               | Memphis, TN                                         | Fluometuron (H-U)                                                                                                                                                                                                                                       | m-trifluoromethylaniline + dimethylamine                                                                                                                                                                                                         | NA                               |
| PPG           | Barberton, OH                                       | Propham (H-C)<br>Furloe (chlorporpham) (H-C)                                                                                                                                                                                                            | aniline + isopropyl alcohol<br>m-Cl-aniline + isopropyl alcohol                                                                                                                                                                                  | 3<br>7                           |
| Shell         | Denver, CO                                          | Methomyl (Nudrin <sup>®</sup> ) (I-C)                                                                                                                                                                                                                   | methylamine + methyl thiomethylketone oxime                                                                                                                                                                                                      | 2                                |
|               | Mobile, AL                                          | Aldicarb (I-C)                                                                                                                                                                                                                                          |                                                                                                                                                                                                                                                  |                                  |
| Stauffer      | Cold Creek, AL<br>St. Gabriel, LA<br>Cold Creek, AL | Eptam <sup>®</sup> (EPTC) <sup>(c)</sup> (H-T)<br>Ordram <sup>®</sup> (molinate) (H-T)<br>Ro-Neet <sup>®</sup> (cycloate) (H-T)<br>Sutan <sup>®</sup> (butylate) (H-T)<br>Tillam <sup>®</sup> (pebulate) (H-T)<br>Vernam <sup>®</sup> (vernolate) (H-T) | ethyl mercaptan + di-n-propylamine<br>ethyl mercaptan + hexamethyleneimine<br>ethyl mercaptan + N-ethyl cyclohexylamine<br>ethyl mercaptan + diisobutylamine<br>n-propyl mercaptan + n-butyl ethylamine<br>n-propyl mercaptan + di-n-propylamine | NA<br>NA<br>NA<br>NA<br>NA<br>NA |
| Union Carbide | South Charleston,<br>WV                             | Sevin <sup>®</sup> (Carbaryl) (I-C)<br>Temik <sup>®</sup> (aldicarb) (I-C)                                                                                                                                                                              | methyl amine + 1-naphthol<br>methyl amine + 2-methyl-2-thiomethyl-N,N-dimethylacetamide                                                                                                                                                          | 100<br>4                         |

(a) H = herbicide, I = insecticide, F = fungicide, U = urea, C = carbamate, T = thiocarbamate

(b) DuPont's capacity is for all urea herbicides.

(c) Also made at St. Gabriel, LA.

| Starting Materials |                   | Products              |                       |
|--------------------|-------------------|-----------------------|-----------------------|
| Reactant 1         | Reactant 2        | Structure             | Class Name            |
| ROH                | -                 | ROCOC1                | chloroformate         |
| ROH                | R'OH              | ROCOOR'               | carbonate             |
| ROH                | R'NH <sub>2</sub> | ROCONHR'              | carbamate or urethane |
| RNH <sub>2</sub>   | -                 | RNCO                  | isocyanate            |
| RNH <sub>2</sub>   | R'NH <sub>2</sub> | RNHCONHR'             | urea                  |
| R <sub>2</sub> NH  | -                 | R <sub>2</sub> NCOC1  | carbamoyl chloride    |
| R <sub>2</sub> NH  | R'NH <sub>2</sub> | R <sub>2</sub> NCONR' | urea                  |
| RSH                | -                 | RSCOC1                | chlorothioformate     |
| RSH                | R'SH              | RSCOSR'               | dithiocarbonate       |
| RSH                | R'OH              | RSCOOR'               | thiocarbonate         |
| RSH                | R'NH <sub>2</sub> | RSCONHR'              | thiocarbamate         |



APPENDIX A

COMPANIES CONTACTED

TABLE A-1. COMPANIES CONTACTED

| Company            | Degree of Interest |           | Comments                                                      |
|--------------------|--------------------|-----------|---------------------------------------------------------------|
|                    | Phosgene           | Cylinders |                                                               |
| Allied             | N                  | N         | Require 99.9%. Purify by Zn filings                           |
| BASF Wyandotte     | M                  | N         | Fe a problem                                                  |
| Rubicon            | M                  | N         | Obtained phosgene free from Mr. Gershon                       |
| Chemetron          | L                  | L         | CCL <sub>4</sub> a problem, condition of valves?              |
| Dow                | N                  | N         | Cl <sub>2</sub> worst contaminant. Add CO and pass over C bed |
| DuPont             | N                  | N         |                                                               |
| FMC                | N                  | N         | Discontinued phosgene production in 1974                      |
| GE                 | N                  | N         | No interest                                                   |
| Texaco (Jefferson) | N                  | N         | No longer producing phosgene or MDI                           |
| Minerec            | M                  | N         | Would bid jointly with Delta who wants cylinders              |
| Mobay              | N                  | N         | Cl <sub>2</sub> is bad, require 99.9% phosgene                |
| Olin               | M                  | N         | Prohibitive cost for redistillation                           |
| PPG                | N                  | N         |                                                               |
| Stauffer           | N                  | N         | Require 99 + % phosgene                                       |
| Story (Cordova)    | N                  | N         | No current interest by Cordova                                |
| Union Carbide      | L                  | N         | Free chlorine is disastrous for TDI                           |
| Upjohn             | N                  | N         | Require very high purity for pharmaceuticals                  |
| Van de Mark        | N                  | N         |                                                               |
| Akzona             | N                  | N         | Purchase chloroformates from Chemetron                        |
| Eastman Kodak      | L                  | N         | Purchase small amounts from Chemetron and Van de Mark         |
| Jakem Indust.      | N                  | N         | Uses 100-pound cyliners                                       |

| Company                 | Degree of Interest |           | Comments                                               |
|-------------------------|--------------------|-----------|--------------------------------------------------------|
|                         | Phosgene           | Cylinders |                                                        |
| Pennwalt                | N                  | N         | Peroxydicarbonates require high purity phosgene        |
| RSA                     | N                  | N         |                                                        |
| Ciba Geigy              | N                  | N         | C-G discontinued phosgene route 10 years ago           |
| Consolidated Chem.      | H                  | H         | They now use 9 cylinders/day                           |
| Gulf                    | N                  | N         | They buy isocyanate from Mobay                         |
| Eli Lilly               | N                  | N         | They use less than 100 lbs./year                       |
| Nor Am Ag.              | N                  | N         | They buy ready-made pesticides                         |
| Shell                   | N                  | N         | Pesticides and intermediates are made by Union Carbide |
| Chem. Commodities       | H                  | H         | Now have guaranteed customer for phosgene              |
| Delta Chem              | L                  | M         |                                                        |
| Jones Chemical          | M                  | H         | Will sell the phosgene                                 |
| Matheson Gas Products   | M                  | N         |                                                        |
| Scientific Gas Products | N                  | N         |                                                        |
| Air Products & Chem     | N                  | N         |                                                        |
| Worthington Steel       | N                  | N         | Produce low pressure cylinders only                    |
| Manley-Regan            | N                  | H         | Interest in storage cylinders for chlorine             |
| Harsco Corp.            | N                  | N         | Small cylinders only                                   |
| Columbiana Boiler       | N                  | N         | Scrap value of cylinders = \$45                        |
| Union Carbide-Linde     | L                  | H         |                                                        |

Source: Battelle interviews.