## ABSTRACT

CYNTHIA STEWART. The Impact of the Decomposition Products of Antispatter Compounds on Welders' Health. (Under the direction of Dr. David A. Fraser.)

In arc and gas welding, metal particles expelled during welding which do not form part of the weld are called spatter. Excessive spatter adjacent to the weld is considered to be a defect and therefore is unacceptable. Antispatter compounds used to prevent spatter build-up (on parent metals, fixtures, welding gun nozzles, contact tips, or electrode holders) may decompose during the welding process to form hazardous gaseous compounds. This study explores the theory that antispatter compounds which contain chlorinated hydrocarbons may decompose to form phosgene (carbonyl chloride). The phosgene concentration created by specific chlorinated hydrocarbons present in various antispatter compounds is investigated. The cause of one welder's illness following the use of an antispatter compound may be implied from the results of the study.

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A. Background to Welding

1. Historical Development

Although the historical development of welding dates back to biblical times, the use of welding is still increasing since it is an economical and efficient way to permanently join metals. Recorded in the book of Genesis approximately 5800 years ago, the first welding process was discovered by a blacksmith named Tubal-Cain when he performed forge welding. Welded tools and artwork dating back to as early as 1000 B.C. may be found in museums around the world. For example, a set of small gold circular boxes, made more than 2000 years ago by pressure welding lap joints together, is presently on exhibit at the National Museum in Dublin, Ireland (8). Forge welding, soldering, and brazing can be traced back to ancient times, but the modern processes of arc welding, resistance welding, and gas welding were discovered in the 1800 's.

An electric arc hot enough to melt an iron wire was first produced in 1800. Sixty years later, an Englishman named Wilde welded two small pieces of iron together with an electric arc. Mr. Wilde received the world's first electric arc welding patent in 1865 (28). The first U.S. patent for
an arc welding process was awarded in 1892. This process was the first where metal melted from the electrode and crossed the arc to deposit filler metal in the joint to make a weld. The oxyacetylene welding and cutting process, the carbon arc welding process, and the metal arc welding process with covered electrodes were perfected during the period of about 1900 to 1918. Gas-shielded arc welding processes, such as gas tungsten arc welding, were developed in the late 1920 's. Since the late 1940 's the processes of plasma arc welding, electron beam, welding, friction welding, and laser welding have been developed (8).

## 2. Description of Welding Processes

The American Welding Society defines welding as "a materials joining process which produces coalescence of materials by heating them to suitable temperatures with or without the application of pressure or by the application of pressure alone and with or without the use of filler material" (5). The welding process may be divided into two main categories: one in which the joint is made by direct fusion of two pieces, and the other in which additional metal is used to make the joint. These two categories may be further divided into specialized processes in which a variety of techniques have been developed in order to produce welds on a wide assortment of metals and alloys under a diversity of conditions and situations (8).

According to the American Welding Society there are more than eighty processes used in welding and cutting. These processes may be placed into seven groups which are defined below.

Arc welding is the group of processes in which coalescence is produced by heating with an electric arc that is generated between an electrode and the surface of the base metal. Shielding of the arc with an inert gas is typically provided to ensure a strongly welded joint.

Brazing refers to the group of processes in which coalescence of materials results from heating these materials to a suitable temperature and utilizing a filler metal with a melting point above $450^{\circ} \mathrm{C}$ and below the melting
point of the base metal. Brazing filler metal is often brass or bronze which is distributed between the surfaces of the join by capillary action. A braze is a special form of a weld in which theoretically the base metal does not melt.

Oxyfuel gas welding processes are those in which coalescence is produced by heating the materials with an oxygenated gas flame or flames. The process may be performed with or without the use of pressure and with or without the use of a filler metal.

The group of welding processes referred to as resistance welding produces coalescence of metals by the heat which evolves from the resistance in an electric circuit. The heat is obtained from the resistance of the work in an electric circuit (in which the work is part of the circuit) and also by the application of pressure.

Soldering is defined as a group of joining processes in which coalescence of materials is produced by heating materials to an appropriate temperature and using a filler metal with a melting point between $450^{\circ} \mathrm{C}$ and the melting point of the base materials. Filler metals are distributed between the surfaces of the joint by capillary attraction.

Solid state welding refers to a group of welding processes that produce coalescence at temperatures which are below the melting point of the base metals to be joined. The process is performed without the use of a brazing filler metal and the use of pressure is optional.

Other welding processes include a miscellaneous group which do not fit into the previous categories. Table I shows the seven groups defined above and the welding processes which fall into each category (5).

Table I
Welding Processes
(5)

| Group | Welding Process | Letter <br> Designation |
| :---: | :---: | :---: |
| Arc Welding | Carbon Arc | CAW |
|  | Flux Cored Arc | FCAW |
|  | Gas Metal Arc | GMAW |
|  | Gas Tungsten Arc | GTAW |
|  | Plasma Arc | PAW |
|  | Shielded Metal Arc | SMAW |
|  | Stud Arc | SW |
|  | Submerged Arc | SAW |
| Brazing | Diffusion Brazing | DFB |
|  | Dip Brazing | DB |
|  | Furnace Brazing | FB |
|  | Induction Brazing | IB |
|  | Infrared Brazing | IRB |
|  | Resistance Brazing | RB |
|  | Torch Brazing | TB |
| Oxyfuel | Oxyacetylene Welding | OAW |
| Gas | Oxyhydrogen Welding | OHW |
| Welding | Pressure Gas Welding | PGW |
| Resistance Welding | Flash Welding | FW |
|  | High Frequency Resistance | HFRW |
|  | Percussion Welding | PEW |
|  | Projection Welding | RPW |
|  | Resistance-Seam Welding | RSEW |
|  | Resistance-Spot Welding | RSW |
|  | Upset Welding | UW |
| Solid State Welding | Cold Welding | CW |
|  | Diffusion Welding | DFW |
|  | Explosion Welding | EXW |
|  | Forge Welding | FOW |
|  | Friction Welding | FW |
|  | Hot Pressure Welding | HPW |
|  | Roll Welding | ROW |
|  | Ultrasonic Welding | USW |

Soldering Dip Soldering ..... DS
Furnace Soldering ..... FS
Induction Soldering ..... IS
Infrared Soldering ..... IRS
Iron Soldering ..... INS
Resistance Soldering ..... RS
Torch Soldering ..... TS
Wave Soldering ..... wS
Other Electron Beam ..... EBWQ
Welding Electroslag ..... ESW
Processes
IW
IW
Laser Beam ..... LBW
Thermit ..... TW
3. Control of Spatter

Spatter is defined as the metal particles expelled during arc and gas welding which do not form part of the weld. Excessive spatter may be caused by arc blow (deflection of the arc from its normal path by magnetic forces), by the selection of the incorrect electrode or welding current, or the technique of the welder. Although spatter may be produced by many welding processes, it is often excessive in gas metal arc welding (GMAW), also referred to as metal inert gas welding (MIG), and $\mathrm{CO}_{2}$ welding. In the MIG welding process the electric current is delivered through a filler wire. As the filler wire constricts when a metal droplet forms, the current density increases very quickly (in an "explosive" manner) as the metal droplet seperates from the wire. This results in the ejection of a spray of very hot metal droplets, and therefore excessive spatter (17). It is not only a laborious operation to remove spatter from the workpiece surface and the torch nozzle, but it is also considered to be a defect (8). Therefore it is desirable to control the production of spatter or provide a simple means for its removal.

Spatter can be minimized by keeping the arc length at the minimum that does not result in electrical shorting. The rate of spatter may also be reduced by using inert shield-gases such as argon or helium, by using welding wires with surface coatings containing no impurities or by using
high inductive power sources which limit the current rise during short-circuiting and therefore reduce the severity of wire "explosions" (17). However, application of protective coatings to the workpiece metal and welding nozzles is the simplest method of reducing adherence and simplifying the removal of spatter $(23,29)$.

Many protective coatings consisting of a wide variety of compounds have been studied. The effectiveness of several coating compositions for protecting against spatter in $\mathrm{CO}_{2}$ welding was investigated in the USSR (29). The protective coatings evaluated were an aqueous solution of chalk and kaolin, an aqueous solution of sulphite and alcohol, and preparations of Duga-1 (ethyl silicate neutralized with alkali), and a silicone lubricant in aerosol form. The coatings were evaluated on their ability to reduce adherence of spatter without impairing the mechanical properties of the weld joints. The results showed that Duga-1 and the silicone lubricant in aerosol form were two to three times more effective for protection against spatter than the aqueous solutions of chalk, kaolin, and sulphite-alcohol wash (29). Antispatter compounds tested in Japan contained alkyd resin emulsion, calcium carbonate, talc, water, and methyl chloroform (31).

Products used in the United States to prevent spatter build-up on the base metal and welding nozzles are commonly referred to as antispatter or antispat. The contents of these products vary from manufacturer to manufacturer. Some
contain silicones, some do not, and some contain chlorinated hydrocarbons and others do not. According to a manufacturer's Material Safety Data Sheet (MSDS) the hazardous ingredients in the antispatter compound were 1,l,l-trichloroethane (methyl chloroform) and carbon dioxide. A second manufacturer's MSDS listed 1,1,1trichloroethane, carbon dioxide, silicone and refined organic oil as hazardous ingredients. The decomposition of
 interest. In order to obtain more specific information about the composition of antispatter compounds used today, two different brands of antispatter compounds were purchased and then analyzed using a Perkin Elmer Sigma 1 Gas Chromatograph. Qualitative and quantitative analyses for chlorinated hydrocarbons were completed and the results are shown in Table II.

## Table II

## Composition of Antispatter Compounds

Compound A
11.32 Trichloroethane
10.85\% Methylene Chloride
0.4 E Ethylene Dichloride
$0.03 \% \mathrm{M}$-Xylene
0.009\% Trichloroethylene

Balance unknown

Compound B
16.77\% Trichloroethane
$0.11 \%$ Methylene Chloride
1.17\% Ethylene Dichloride
0.06 \% M-Xylene
0.01\% Trichloroethylene

Balance unknown

## B. Case Study

The cause of one welder's illness may be related to the use of an antispatter compound. A 54-year-old white male previously in excellent health, experienced tightness in his chest and coughing after welding galvanized steel playground equipment. A chest x-ray disclosed a mottled pattern through both lung fields. The biopsy revealed that this pattern was caused by wide-spread multiple lesions resulting from chemical burns. Further observation disclosed that a fume particle or agglomeration of particles was surrounded by a very large burned area. The mechanism of this occurrence was identified as the combined effect of the metallic fume and the possibility that the fume was coated or impregnated with a caustic component, most likely a chlorinated species such as phosgene. The diagnosis ultimately revealed that the welder had developed fibrosis.

The welding process being used was metal arc welding, also referred to as continuous wire electrode welding. An antispatter product was being applied abundantly as the welding process was being performed, to provide a smooth welding joint. A more common practice is to apply the antispatter product and allow it to dry before proceeding with welding. The antispatter product contained methylene chloride which may have decomposed to form phosgene. Inhalation of phosgene may cause acute bronchitis, acute bronchiolitis, pulmonary edema, emphysema, fibrosis, or death.
C. Hazards in the Welding Environment

Man's progress is often marred by unpredictable secondary effects. Man's ingenuity and ability to weld has enabled him to build bridges, ships, space vehicles, automobiles, pipelines, and even microcircuits. During this time of progress and invention it became apparent that there were many health and safety hazards related to welding. The following discussion will simply identify some of the hazards and their potential effects on the welder's health. Awareness of these hazards is the first step in providing protection to the welder in the workplace.

1. Fumes

Fumes are small, solid particles created by condensation from the gaseous state, generally after volatilization followed by a chemical reaction such as oxidation. The sources of fumes created during the welding process may be the base metal, the flux, or the core wire. Table III shows some examples of metal fumes and their sources (7). The rate of fume generation in any welding process is affected by the welding current, arc voltage, arc temperature, electrode polarity, electrode diameter, speed of welding, and welding practices (4). The potential harm from exposure to fumes depends on the chemical composition of the fumes, the concentration in the welder's breathing zone, the length of exposure, and many other factors such as the size, density, and surface area of the particle. Many studies

## Table III

## Fumes and Their Sources (7)

Metal Fumes

Iron

Chromium

Nickel
zinc
Copper

Vanadium, manganese, and molybdemun

Tin
Cadmium
Lead
Fluorides

Parent iron or steel metal, electrode

Stainless steel, electrode, plating, chromate primed metal

Stainless steel, nickel-clad steel

Galvanized or zinc primed steel
Coating on filler wire, sheaths on air-carbon arc gouging electrodes, nonferrous alloys

Welding rod, alloys in steel

Tin coated steel
Plating
Lead paint, electrode coating
Flux or electrodes
have been done to determine the effects of exposure to fumes.

The particle size distribution is an important factor in determining the hazard potential of welding fumes. It is an indication of the depth to which particles may penetrate into the respiratory system and it is also an indication of the percentage of particles that will remain in the respiratory system as well as the surface area presented for reaction with biological fluids. Welding fumes are almost all less than one micrometer ( 1 um) in diameter (1). Particles in the range of 1 to 7 um in diameter represent a serious hazard due to penetration into the alveolar region of the lungs. Although most welding fume particles are less than 1 um in diameter when formed, results of one study indicate that they may agglomerate and increase in size with time (9).

The workpiece metal for a majority of welding processes is mild steel. Therefore, the major component of welding fumes is often iron, usually in the form of iron oxide. Inhalation of iron oxide fumes over an extended period of time may cause a condition known as siderosis, a benign form of pneumoconiosis. Pneumoconiosis is defined as the accumulation of "dust" in the lungs and the tissue reaction to its presence. There is no disability or proliferation of fibrous tissue resulting from exposure to iron oxide fumes, and therefore diseases such as emphysema and fibrosis do not develop (14).

A condition known as metal fume fever may be caused by metals such as copper, zinc, and manganese which may be present in welding fumes. High fever is accompanied by coughing, shortness of breath, weakness, fatigue, and pains in the muscles and joints. Symptoms may occur for 24 to 48 hours and then subside. Zinc from galvanized steel and pigments and decomposition products from welding on painted surfaces may be encountered frequently (14). Some fume constituents may pose more of a potential hazard than others, depending on their toxicity. Of special concern are silica or silicates, fluorides, copper, chromium, nickel, and manganese. Table IV lists these and other metals or compounds found in welding fumes, along with some typical effects on the body $(14,20)$.
2. Gases

Gases are produced in all welding processes. The principal gases produced in arc and oxygas welding are ozone, nitrogen oxides, and carbon monoxide. The presence of chlorinated hydrocarbons in the welding environment may result in the decomposition of these hydrocarbons to form phosgene, hydrogen chloride, or dichloroacetyl chloride (13). Many studies have been completed to identify the mechanism of formation for the gases mentioned above. Additional studies to determine the health effects of exposure to these gases have also been completed. Table V lists the various gases and their effect on the body (14).

Table IV
Fumes and Their Effects on the Body $(14,20)$

| Metal/Compound $\qquad$ | Acute Effect | Chronic Effect |
| :---: | :---: | :---: |
| Cadmium | Pulmonary irritation and edema | Emphysema, kidney, damage |
| Chromium | Skin irritation | Increase risk of lung cancer |
| Copper | Irritation of nose and throat, nausea, metal fume fever | None known |
| Fluorides | ```Eye, nose, throat irritation, pulmo- nary edema, skin rash``` | Bone changes |
| Iron | Irritation of nose throat, and lungs | Siderosis (benign pneumoconiosis) |
| Manganese | Metal fume fever | Central nervous system problems |
| Lead | None known | Anemia, fatigue, abdominal pains, reduced fertility, kidney and nerve damage |
| Nickel | Eye, nose and throat irritation | Increased cancer risk |
| $\begin{aligned} & \text { Silica/ } \\ & \text { silicates } \end{aligned}$ | None known | Silicosis (pulmonary fibrosis) |
| Tin | None known | Stannosis (benign pneumoconiosis) |
| Vanadium | Irritation of eyes, skin, and respiratory tract | ```Bronchitis retinitis, pulmonary edema, and pneumonia``` |
| Zinc | Metal fume fever | None known |

## Table V

Gases in the Welding Environment (4)

| Gas | Formation Mechanism | Acute Effects | Chronic Effects |
| :---: | :---: | :---: | :---: |
| Oz one | Photochemical reaction by ultraviolet <br> radiation and oxygen | Pulmonary congestion, edema, and hemorrhage | Emphy sema |
| Nitrogen Oxides | Photochemical reaction by ultraviolet radiation | Pulmonary congestion and edema | Emphy sema |
| Carbon Monoxide | Decomposition of electrode coating or flux material | Headache, dizziness, mental confusion | None known |
| Phosgene | Decomposition of chlorinated hydrocarbons | Pulmonary edema | Bronchitis, Fibrosis Emphy sema |
| Hydrogen Chloride | Decomposition of chlorinated hydrocarbons | Irritation of eyes, nose, and throat | Bronchitis |
| Dichloroacetyl chloride | De composition of chlorinated hydrocarbons | Irritation of skin and eyes | None Known |

3. Radiation

Most welding processes emit electromagnetic radiation from the ultraviolet, visible, and infrared portions of the light spectrum. All three forms present a hazard to the welder and to those working in the vicinity of welding (4).

Ultraviolet radiation may effect both the eyes and the skin. The following effects to the eye may occur from exposure: 1) inflammation of the cornea and conjunctiva referred to as "arc eye" or "flash burns" by welders; 2) retinal lesions; 3) yellowing of the lens; and 4) cataracts. Ultraviolet exposure to the skin may cause reddening of the skin (erythema), blistering, or in extreme cases complete destruction of tissue and ultimately bleeding. Long term exposure to ultraviolet radiation increases the risk of skin cancer (21). If the visible light is very intense, fatigue to the muscles used to squint may occur and infrared light may be felt as heat, but may also affect the eyes (3).
4. Noise

Most welding processes generate noise levels which may vary greatly depending on the welding process being used. One study concluded that the most quiet was the gas tungsten arc process and the most noise was generated by the air carbon arc process. Processes such as arc gouging, plasma arc cutting, air carbon arc cutting, and grinding were identified as those generating excessive noise levels. For example, the sound pressure levels measured for arc
gouging processes range from 95 to 115 dBA (19). Welding machines and additional equipment in the welder's vicinity also create noise that increase the sound level to which the welder is exposed (4).
5. Electrical

The energy required for melting metals to obtain coalescence in most welding processes is provided through an electric arc. This electricity is distributed by what is commonly referred to as a welding machine. Welding machines can be designed to use either alternating current (AC) or direct current (DC). Power for AC machines is provided through transformers using line voltage. DC machines may be powered by a rotating generator or by a transformer/ rectifier system (3). The obvious hazard when working with electricity is the risk of electrical shock. Inadequate grounding of equipment, worn or damaged cables or electrode holders, lack of proper gloves, and wet conditions can greatly increases the risk to the welder. Other factors that may affect the risk include: 1) type of circuit; 2) voltage, 3) path of current through the body; 4) current level; and 5) duration of contact. The risk to the body is much greater when the flow travels through the trunk than when it remains in the extremities (3). Safety guidelines and procedures to prevent accidents involving electricity must be a part of every welder's training.
6. Fire/Explosion

Welding processes provide all the elements necessary for fires. Fires and explosions have been caused by welding when sparks have traveled up to forty feet, fallen through cracks or pipe holes in the floor, or hot pieces of the base metal have come in contact with combustible materials. If heat from the welding process is transmitted through walls of containers to flammable atmospheres or to combustibles, the result can be fire or explosion. Anything that is flammable or combustible is susceptible to ignition by welding (8).

Welding fires can be prevented by eliminating combustibles from the welding area and welding should only be performed in non-flammable atmospheres. Special work procedures for welding in confined spaces should be used. Additional procedures for welding on equipment containing flammables should be followed by the welder (3). 7. Other Factors

Welding processes provide a vast array of hazards and a few additional factors may be mentioned. An obvious problem that has not been discussed is the risk of being burned. Thermal burns to the skin from hot metal, spattered slag, or from handling hot tools or electrodes are quite common. Heat may present a problem when welding is done in confined spaces or when the metal has been preheated to improve welding characteristics. All compressed gas cylinders are potential hazards because sudden release of
turn the cylinder into a projectile. Welders burdened with goggles, face shields, and other protective equipment may be more subject to hazards such as trips, slips, falls and the many other potential hazards in any work environment.
II. PROBLEM
A. Decomposition of Chlorinated Hydrocarbons

1. Use of Chlorinated Hydrocarbons

The use of chlorinated hydrocarbons is extensive in today's industries. Many of these chlorinated hydrocarbons are used as solvents in a variety of applications such as the degreasing and cleaning of metals or the dry cleaning of clothes. They are also used in the textile industry, as refrigerants, and even as an extraction solvent for the decaffeination of coffee, spices, and beer hops (18). It is apparent from the wide range of uses that these chlorinated hydrocarbons can be present in areas where maintenance, repair, and construction are performed. Therefore, these chlorinated hydrocarbons may be present where open arc welding is being used to join metals.
2. Decomposition in the Welding Environment

Phosgene, hydrogen chloride, carbon monoxide, and dichloroacetyl chloride form during welding if degreasing agents containing chlorine come into contact with the welding flame or are exposed to the radiation from the electric arc (16). A few studies have been done to determine the factors of the welding process that may affect the concentration of the compounds mentioned above as they
form in the welding environment. In addition, three studies to determine the solvent that may present the least hazard in the welding environment have been reported. The conclusions of these studies were not always in agreement, but knowledge obtained from the data was useful.

Many factors such as characteristics of the welding arc and chemical properties of the chlorinated hydrocarbon will decompose in the welding environment. The chlorinated hydrocarbons are decomposed both by heat and ultraviolet radiation from the welding arc. Studies in which the vapors of chlorinated hydrocarbons in air have been passed over heated metals have been performed to determine decomposition products. When chlorinated methane, ethane, and ethylene compounds were heated over various substances, carbon tetrachloride always produced the most phosgene and the extent of phosgene formation decreased with decreasing chlorine content in the chloromethane compounds. Chlorinated ethanes which contain at least one hydrogen atom produced chloroform, or hexachloroethane (10).

It is often stated that the decomposition of chlorinated hydrocarbon solvents occurs in the ultraviolet field around the welding arc. The decomposition products of trihcloroethylene were investigated and the following observations were made: 1) The main decomposition product is dichloroacetyl chloride and it forms three times as fast as phosgene. 2) The decomposition rate decreases rapidly as the trichloroethylene concentration decreases and the
distance from the arc increases. 3) The decomposition rate appears to increase when the gas metal-arc process, instead of the gas-tungsten arc process is used for welding (13). The most intense emission of ultraviolet radiation is produced by argon-shielded arcs. The short-wave band of the ultraviolet spectrum present in argon shields is of special importance in the decomposition of chlorinated hydrocarbons. Ultraviolet radiation from welding arcs in the wavelength interval between 1900 to 2900 angstrom units (A) is significant to decomposition because most solvents, including chlorinated hydrocarbons, have their main absorption bands below 2900 A. It is interesting to note that the spectrum of the arc is essentially determined by the main component of the welding electrode and also that the intensity of the ultraviolet emission from the arc increases with current strength (11). The decomposition of chlorinated hydrocarbons is very complex and various chemical properties may also play a role.

The chemical structure, including the bonding and number of chlorine atoms, influence the formation of phosgene. The main absorption band for ultraviolet radiation of each chemical is important in the welding environment. The vapor pressure of the chlorinated hydrocarbon may be significant because the chemicals with higher vapor pressures may result in high concentrations of chemical vapors near the welder. The rate of dichloroacetyl chloride and phosgene formation was dependent on the partial pressure of trichloroethylene
because the amount of ultraviolet radiation absorbed was also dependent on the partial pressure of trichloroethylene (13). However, this dependence was not observed when experiments with methyl chloroform were performed (12). The decomposition of chlorinated hydrocarbons in the welding environment is a very complex process.
B. Health Effects of Exposure to Phosgene

Table VI lists some physical properties and exposure limits for phosgene (20). Phosgene $\left(\mathrm{COCl}_{2}\right)$ is a colorless gas at standard temperature and pressure. At low concentrations its odor has been described as resembling that of musty hay or green corn. It is an irritant gas which may cause pulmonary edema as a result of acute exposure or irreversible pulmonary changes of emphysema and fibrosis as a result of chronic exposure. Upon inhalation in moderate dosage, phosgene, only slightly soluble in water, does not react noticeably with the aqueous mucus film of the upper respiratory tract, and therefore reaches the alveolar region of the lung, resulting in immediate and irreversible damage. Phosgene may irritate the skin and eyes, but its irritant effects are not sufficient to give warning of hazardous condition (2).

Inhalation is the most significant route of exposure to phosgene. The toxic effects of phosgene are caused by the hydrolysis of the material at the cell site producing hydrochloric acid and carbon dioxide (15). The chemical equation for this hydrolysis is shown below:

$$
\mathrm{COCl}_{2}+\mathrm{H}_{2} \mathrm{O} \longrightarrow 2 \mathrm{HCl}+\mathrm{CO}_{2}
$$

Only a relatively small portion of phosgene hydrolyzes in the respiratory passages, but in the terminal end of the

Table VI. Physical Properties of Phosgene (20)

Chemical: Phosgene
Synonyms: Carbonyl chloride, carbonic acid dichloride, carbonyl dichloride, chloroformyl chloride, carbon oxychloride, combat gas

CAS Reqistry No.: 75-44-5
Physical Properties:
Molecular Formula: $\quad \mathrm{COCl}_{2}$
Molecular Weight: 98.92
Melting Point, ${ }^{\circ} \mathrm{C}: \quad-128$ to -104
Boiling Point, ${ }^{\mathrm{O}} \mathrm{C}$ at $1 \mathrm{~atm}: \quad 7.5$ to 8.3
Density at $20^{\circ} \mathrm{C}, \mathrm{g} / \mathrm{cm}^{3}$
1.387

Vapor Density (air = 1.0) 3.4
Vapor Pressure at $20^{\circ} \mathrm{C}$, kPa 161.68
Conversion Factors:

Color:
Odor:

Flammability:
Solubility:
$1 \mathrm{mg} / \mathrm{m}^{3}=0.25 \mathrm{ppm}$
$1 \mathrm{ppm}=4.1 \mathrm{mg} / \mathrm{m}^{3}$
Colorless
Sweet in low concentrations
Pungent in high concentrations
Nonflammable
Decomposes in water, alcohol
Very soluble in benzene,
toluene

Exposure Limits:
OSHA-PEL
ACGIH-TLV

$$
\begin{array}{ll}
0.1 \mathrm{ppm} & \left(0.4 \mathrm{mg} / \mathrm{m}^{3}\right) \\
0.1 \mathrm{ppm} & \left(0.4 \mathrm{mg} / \mathrm{m}^{3}\right)
\end{array}
$$

alveoli complete hydrolysis occurs with disastrous effects on the alveolar walls and blood capillaries. The result of this action is a gradually increasing edema, until as much as fifty percent of the total plasma from the alveolar walls and lung blood capillaries may accumulate in the lungs. The active air spaces decrease in number, which decreases oxygen exchange and weakens the heart and other oxygen deprived tissue. The end result may be either asphyxiation or heart failure (6). In December 1915, the Germans introduced phosgene as a poison gas, which was responsible for eighty percent of the gas casualties in World War I (22).

Another product resulting from the decomposition of some chlorinated hydrocarbons is dichloroacetyl chloride. There is very little toxicological data for dichloroacetyl chloride and no exposure limits have been determined. It is a fuming liquid with an acrid odor and is moderately irritating to the skin, eyes, and respiratory system (24).

The purpose of this study was to investigate the potential risk of exposure to hazardous concentrations of phosgene from the decomposition of chlorinated hydrocarbons in antispatter products used during welding. A controlled experiment performed in a chamber was used to verify that chlorinated hydrocarbons can decompose to form phosgene and that these chlorinated hydrocarbons, as part of the antispatter compound, decompose to form phosgene. In addition, air samples were taken in a small welding shop as a welder used the antispatter products. The measured phosgene concentrations were then to be interpreted in the evaluation of one welder's illness following the use of an antispatter compound.

## IV. DESCRIPTION OF THE STUDY

A. Controlled Experiments

The controlled experiments were performed in a plexiglass chamber with a volume of 1160 liters. Analysis of the antispatter compounds using gas chromatography revealed that the compounds contained methylene chloride and methyl chloroform. Each of these chemicals was injected into the chamber for individual trials in volumes to create a concentration of one, one-half, or one-tenth of the American Conference of Governmental Industrial Hygienist's (ACGIH) Threshold Limit Value (TLV). The volume of methylene chloride or methyl chloroform to be injected into the chamber was determined using the following equation:

$$
\begin{aligned}
\text { Conc }(\mathrm{ppm})= & \{[(\mathrm{Vx})(\mathrm{p})(22.4 / \mathrm{MW})(\mathrm{T} / 273)(760 / \mathrm{P})] /(\mathrm{Vt})\} \\
& \times 100000
\end{aligned}
$$

where:

$$
\begin{aligned}
\mathrm{Vx} & =\text { volume of material to be used (ml) } \\
\mathrm{p} & =\text { density (grams/ml) } \\
\mathrm{Vt} & =\text { chamber volume (liters) }
\end{aligned}
$$

The chemical was injected onto a glass dish in the chamber and a small fan located inside the chamber enhanced evaporation and mixing.

Analysis of the contaminants in the chamber was performed using a single-beam infrared spectrometer. The instrument was able to scan the infrared spectrum from 2.5 um to 14.5 um and the pathlengths available in the gas cell ranged from 0.75 to 20.25 meters. The Foxboro Miran 1A Portable Gas Analyzer (Serial Number 1A 916) was calibrated for methylene chloride, methyl chloroform phosgene, and dichloroacetyl chloride. The instrument was then connected in a closed loop system with the chamber. When the infrared instrument indicated a stable absorbance value for methylene chloride or methyl chloroform (depending on which chemical had been injected into the chamber) the wavelength and pathlength parameters were changed for analysis of phosgene or dichloroacetyl chloride. A propane torch was then lit and held so that the nozzle of the torch fit through a small opening in the chamber and the flame burned in an atmosphere containing a contaminant. The flame burned for two minutes and was then removed. When the infrared instrument reached a stable absorbance reading, the torch was lit and placed in the chamber for another two minutes. A total of six twominute burning times were performed. As a preliminary step, relatively large volumes of methylene chloride or methyl chloroform were injected into the chamber and the torch flame burned to verify that these solvents did decompose
under the conditions provided to form phosgene. The sequence of two-minute burning times was completed for methylene chloride at one, one-half, and one-tenth the TLV, for methyl chloroform at one, one-half, and one-tenth the TLV, and for each of the two antispatter compounds (injected into the chamber as a liquid form in a syringe). Experiments were performed to determine phosgene concentrations and experiments were performed to determine dichloroacetyl chloride concentrations.

A variation of the procedure discussed above was used to investigate the effects of heating various metals in relation to the phosgene production. Instead of simply introducing the flame into the chamber, the flame was used to heat a one inch square piece of metal. The metals used were aluminum (a three inch square piece was used because the smaller square melted), brass, cold rolled steel, galvanized steel, stainless steel, and titanium. The sequence of six two-minute burning times was followed and the infrared instrument was used to determine phosgene concentrations.

Two other variations were performed to simulate the actual use of the antispatter compound as an aerosol spray. The antispatter compound was sprayed into the chamber and the torch flame was introduced into the chamber for two minutes. The phosgene concentration was then noted. Then the antispatter compound was sprayed on the one inch square piece of metal and the torch flame was then used to heat the
coated metal. Again, the phosgene concentration was noted following the two-minute burning time.

In an attempt to verify the precision and accuracy of the infrared instrument, it was compared to other methods for determining phosgene concentrations. Simultaneous measurements were performed using the infrared instrument and the National Institute for Occupational Safety and Health's (NIOSH) method for measuring phosgene in air. The NIOSH method is a colorimetric method in which impingers containing a solution of 4,4 -nitrobenzyl pyridine in diethyl phthlate reacts with trace amounts of phosgene to produce an orange color (27). The analysis of the impinger solutions were performed by the experimenter using a Bausch and Lomb spectrophotometer. The performance of the infrared instrument was also compared to Draeger colorimetric detector tubes for phosgene (Catalogue Number CH 28301). The detector tubes were used to measure phosgene concentrations in the chamber which were being determined by the infrared instrument at the same time.
B. Field Study

In an attempt to simulate the use of antispatter compounds in the occupational setting, some trials were performed in a welding shop by a skilled welder. The welding shop had a volume of approximately 3888 cubic feet or 110,100 liters. Exhaust ventilation was available, but was not used during the investigation. The antispatter compounds were used as specified by the manufacturer's directions and gas tungsten arc welding (TIG) was used to join various metals. Three metals, mild steel, stainless steel, and aluminum, were used in order to investigate the effects of various metals on the phosgene concentration produced during welding. Phosgene concentrations were measured using the infrared instrument and a few Draeger detector tubes for phosgene were also used. Sampling was done at approximately three inches above the base metal to determine the "worst case" exposure.

## V. RESULTS AND DISCUSSION

A. Controlled Experiments

Initially, the decomposition of methylene chloride and methyl chloroform to phosgene was verified. This was done by measuring phosgene concentrations with the infrared instrument and the NIOSB colorimetric method following a two-minute burning period with the torch. Table VII shows the results of the various trials and the difference between the concentrations indicated by the infrared instrument and the NIOSH method. The concentrations determined using the infrared instrument were consistently about $13 \%$ higher than the concentrations determined using the NIOSH method. A clear-cut explanation for this difference is not obvious, but the accuracy and precision of the NIOSH method have not been determined. However, it has been determined that the NIOSH method is not subject to interference from chloride, hydrogen chloride, chlorine dioxide, or simple chlorinate hydrocarbons. Further study revealed that acid chlorides may produce color with the sampling reagent (30). These factors merely show the complexity of problems that must be considered while using this sampling method.

The results of the sequence of two-minute burn times for methylene chloride are shown in Table VIII. Both the

Table VII
Verification of Decomposition Products Variation of Results with Method

| $\begin{aligned} & \text { Chemical } \\ & \text { Added } \end{aligned}$ | Volume Added to Chamber $\qquad$ (ul) | Theoretical <br> Methylene Chloride Conc (ppm) | Phosgene Conc Indicated by IR Instrument (ppm) | Phosgene Conc Indicated by NIOSH Method $\qquad$ (ppm) $\qquad$ | \% Differen Between <br> IR Instrum $\qquad$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| Methylene Chloride | 100 | 33.2 | 0.41 | 0.36 | 13.9 |
| Methylene Chloride | 200 | 66.3 | 1.65 | 1.48 | 11.5 |
| Methylene Chloride | 300 | 99.5 | 1.60 | 1.40 | 14.3 |
| Methyl Chloroform | 2000 | 423 | 3.8 | 3.4 | 11.8 |
| Methyl Chloroform | 300 | 635 | 4.4 | 3.9 | 12.8 |

Table VIII
Results of Two-Minute Burn Sequence for Methylene Chloride

| Cumulative Burn Time $\qquad$ | Methylene <br> Chloride <br> One TLV=100 ppm Phosgene Conc (ppm) | Methylene Chloride $1 / 2 \mathrm{TLV}=50 \mathrm{ppm}$ Phosgene $\qquad$ Conc (ppm) | ```Methylene Chloride 1/10 TLV=10 ppm Phosgene Conc (ppm)``` | Methylene Chloride One TLV=100 ppm Dichloroacetyl <br> Chloride Conc (ppm) |
| :---: | :---: | :---: | :---: | :---: |
| 2 | 3.0 | 1.35 | 0.11 | 1.0 |
| 4 | 5.0 | 2.27 | 0.43 | 1.8 |
| 6 | 6.1 | 2.9 | 0.63 | 2.5 |
| 8 | 6.9 | 3.4 | 0.73 | 3.3 |
| 10 | 7.3 | 3.6 | 0.83 | 4.1 |
| 12 | 7.5 | 3.7 | 0.95 | 4.9 |

phosgene and dichloroacetyl chloride concentrations are provided. The phosgene and dichloroacetyl chloride concentrations increased as the time of burning increased, but the rate of phosgene or dichloroacetyl chloride production decreased as the burn time increased. For example, during the first two-minute burn under the one TLV column, 3.0 ppm phosgene were produced, but during the last two-minute burn only 0.2 ppm of phosgene was produced. A decrease in the phosgene concentration generated corresponded to lower initial concentrations of methylene chloride.

Figure 1 shows the increase of phosgene concentration that results from the increasing burn time and the increase of the initial methylene chloride concentration. Figure 2 also shows the increase of phosgene concentrations with time and initial methylene chloride concentration and also shows the decrease in the rate of phosgene production over time. All of the phosgene concentrations were greater than the TLV for phosgene, which is 0.1 ppm (2). There is no TLV for dichloroacetyl chloride. Table VIII shows that the dichloroacetyl chloride concentrations were approximately one-third to one-half the values noted for phosgene, when the initial concentrations of methylene chloride were equal. However, the rate of dichloroacetyl chloride generation did not seem to decrease with time as did the rate of phosgene generation.

Fig. 1 - Two-Minute Burn Sequence Methylene Chloride


Fig. 2 - Two-Minute Burn Sequence Methylene Chloride


Table IX
Results of Two-Minute Burn Sequence for Methyl Chloroform

| Cumulative Burn Time $\qquad$ | Methyl <br> Chloroform <br> One TLV=350 ppm Phosgene Conc (ppm) | Methylene Chloroform $1 / 2 \mathrm{TLV}=175 \mathrm{ppm}$ Phosgene $\qquad$ Conc (ppm) | Methylene Chloroform $1 / 10 \mathrm{TLV}=35 \mathrm{ppm}$ Phosgene $\qquad$ Conc (ppm) | Methyl Chloroform One TLV $=350 \mathrm{ppm}$ Dichloroacetyl Chloride Conc (ppm) |
| :---: | :---: | :---: | :---: | :---: |
| 2 | 5.1 | 2.6 | 0.6 | 2.8 |
| 4 | 8.7 | 4.0 | 1.0 | 4.4 |
| 6 | 11.0 | 5.0 | 1.4 | 4.8 |
| 8 | 12.8 | 5.8 | 1.7 | 5.1 |
| 10 | 14.2 | 6.5 | 2.0 | 5.6 |
| 12 | 15.2 | 7.4 | 2.1 | 5.8 |

Table IX shows the results of the sequence of two-minute burn times for methyl chloroform. The phosgene and dichloroacetyl chloride concentrations increased with the increase of burning time, but the rate of generation for both decreased with the increasing burn time. As the initial methyl chloroform concentration decreased, the concentration of phosgene generated decreased. None of the phosgene concentrations produced was less than its TLV of 0.1 ppm. The concentrations of dichloroacetyl chloride produced were approximately one-third to one-half the concentrations of phosgene produced, when starting with the same initial concentration of methyl chloroform.

Pigure 3 shows the increase of the phosgene concentration with increasing burn time and also with increasing the initial methyl chloroform concentration. Figure 4 shows the increase of phosgene concentrations with increasing time and methyl chloroform concentration, and also shows the decrease in the rate of phosgene production over time.

The purpose for using concentrations of one, one-half, and one-tenth of the TLV was to investigate the possibility of exceeding the TLV for phosgene while being at concentrations below the TLV for methylene chloride or methyl chloroform. As shown in Table VIII and Table IX, concentrations much greater than the TLV for phosgene were produced at fractions of the TLV for methylene chloride and methyl chloroform. This leads one to question the safety of

Fig. 3 - Two-Minute Burn Sequence Methyl Chloroform


Fig. 4 - Two-Minute Burn Sequence Methyl Chloroform

welding in an environment containing these solvents at concentrations near their TLV. In fact this has been investigated and it has been determined that trichloroethylene, perchloroethylene, and methyl chloroform, when present in air near welding operations, may be decomposed to dangerous levels of phosgene (12). It is recommended that if welding has to be done in environments containing these solvents, that a welding booth should be equipped with both a fresh air intake and a vent, and should be kept slightly above the pressure of the surroundings to prevent air contaminated with solvent from getting inside the booth $(12,25)$.

In a study that was mentioned previously (13), it was established that phosgene was not the main product in the photochemical oxidation of trichloroethylene, but dichloroacetyl chloride. The dichloroacetyl chloride yield was usually five times that of phosgene. It was also stated that dichloroacetyl chloride formed three times as fast as phosgene (13). The results for methylene chloride and methyl chloroform from this study do not agree with these observations. The results shown in Table VIII and Table IX indicate that the dichloroacetyl chloride yield during the decomposition of methylene chloride or methyl chloroform was one-third to one-half the yield for phosgene. These differences may be the result of various factors in the study design such as the solvent chosen for study (trichloroethylene versus methylene chloride or methyl
chloroform), the method used to cause photochemical oxidation (welding versus a propane torch), and the experimental setting (small room versus a chamber). The two studies both indicated that as the initial concentration of chlorinated hydrocarbon increased the rate and concentration of phosgene and dichloroacetyl chloride also increased.

The odor of dichloroacetyl chloride is very penetrating and may be recognized at a concentration of 0.1 ppm . A dichloroacetyl chloride concentration of 10 ppm will immediately cause coughing and eye irritation and is not endurable for very long (13). Therefore, in the case of trichloroethylene, exposure to phosgene concentrations greater than 2 ppm or higher for longer than a few minutes would be very unlikely. Unfortunately this does not appear to hold true for methylene chloride and methyl chloroform. If one detects dichloroacetyl chloride while working near methylene chloride or methyl chloroform, it would be best to vacate the area since the phosgene concentration is most likely to be two to three times greater than the dichloroacetyl chloride concentration. During the various trials in the chamber, the odor of dichloroacetyl chloride was often detected when the cork was removed from the side wall of the chamber to allow the torch to be moved in and out of the chamber.

At equal increments of the TLV for methylene chloride and methyl chloroform the phosgene and dichloroacetyl chloride concentrations produced were greater for methyl
chloroform. However, the TLV for methyl chloroform is 350 ppm and the TLV for methylene chloride is 100 ppm (2). At equal initial concentrations, methylene chloride would produce greater concentrations of phosgene than methyl chloroform. This is made apparent by comparing the results in Table XIII and Table IX for methylene chloride at 100 ppm and methyl chloroform at 175 ppm . In this example, the phosgene concentrations created from methylene chloride were greater, even though the initial concentration of methylene chloride was less than the initial concentration of methyl chloroform. This relationship is clearly shown in Figure 5. For methylene chloride and methyl chloroform concentrations at the TLV, the concentrations of dichloroacetyl chloride generated were greater for methyl chloroform.

Results of the effects that heating metals may have on the generation of phosgene from the decomposition of methylene chloride or methyl chloroform are shown in Table X and Table XI. The mass of each metal square is noted in the headings of Table $X$ and Table XI. The heat of the torch was usually high enough that the metals were glowing red. The concentrations of phosgene created during the heating of metals in atmospheres containing methylene chloride or methyl chloroform were less than phosgene concentrations generated while simply burning the torch and not heating metals. When the torch flame was focused on the small piece of metal a smaller volume of contaminated air may have


Table X
Phosgene Concentration: Effects of Heated MetalsInitial Methylene Chloride Concentration of One-half $T L V=50 \mathrm{ppm}$

|  | No | Cold Rolled | Titaniu | Brass | Aluminum | Galvanized | Stainless |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Cumulative | Metal | (4.4 g) | (3.1 g) | (3.9 g) | $(25.6 \mathrm{~g})$ | $(3.6 \mathrm{~g})$ | (4.2 g) |
| Burn Time | Phosgene | Phosgene | Phosgene | Phosgene | Phosgene | Phosgene | Phosgene |
| (min) | Conc (ppm) | Conc (ppm) | Conc (ppm) | Conc (ppm) | Conc (ppn) | Conc (ppm) | Conc (ppn) |


| 2 | 1.35 | 0.53 | 0.83 | 0.58 | 0.70 | 0.95 | 0.75 |
| ---: | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| 4 | 2.27 | 1.18 | 1.47 | 1.27 | 1.11 | 1.99 | 1.35 |
| 6 | 2.9 | 1.7 | 1.8 | 1.7 | 1.6 | 2.55 | 1.74 |
| 8 | 3.4 | 2.0 | 2.0 | 2.0 | 1.9 | 2.9 | 2.05 |
| 10 | 3.6 | 2.2 | 2.3 | 2.3 | 2.1 | 3.0 | 2.2 |
| 12 | 3.7 | 2.3 | 2.4 | 2.5 | 2.2 | 3.1 | 2.3 |

Table XI
Phosgene Concentration: Effects of Heated MetalsInitial Methyl Chloroform Concentration of One-half TLV $=175$ ppm

|  | Cold Rolled |  |  |  |  |  | Galvanized Stainless |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | No | Steel | Titanium | Brass | Aluminum | Steel | Steel |
| Cumulative | Metal | $(4.4 \mathrm{~g})$ | $(3.1 \mathrm{~g})$ | $(3.9 \mathrm{~g})$ | $(25.6 \mathrm{~g})$ | $(3.6 \mathrm{~g})$ | $(4.2 \mathrm{~g})$ |
| Burn Time | Phosgene | Phosgene | Phosgene | Phosgene | Phosgene | Phosgene | Phosgene |
| (min) | Conc (ppm) | Conc (ppm) | Conc (ppm) | Conc (ppm) | Conc (ppm) | Conc (ppm) | Conc (ppm) |


| 2 | 2.6 | 1.6 | 1.1 | 1.0 | 0.80 | 1.2 | 1.3 |
| ---: | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| 4 | 4.0 | 2.7 | 2.1 | 1.85 | 1.94 | 2.6 | 2.2 |
| 6 | 5.0 | 3.7 | 3.0 | 2.7 | 2.4 | 3.25 | 2.9 |
| 8 | 5.8 | 4.4 | 3.5 | 3.3 | 2.8 | 3.75 | 3.55 |
| 10 | 6.5 | 4.8 | 4.0 | 3.7 | 3.3 | 3.9 | 3.85 |
| 12 | 7.4 | 5.3 | 4.1 | 3.9 | 3.5 | 4.0 | 4.1 |

Fig. 6 - Effect of Heated Metals


Fig. 7 - Effect of Heated Metals

passed through or near the flame and therefore there may be less decomposition of the solvent to phosgene. Figure 6 and Pigure 7 show that the phosgene concentrations did increase with increasing burning time, but the rate of this phosgene generation decreased with time. Figure 6 and Figure 7 also show that there were no identifiable patterns as to which metal may have had the greatest or least influence on the phosgene concentrations generated.

It is interesting to compare the results obtained in this experimental setting to other similar projects. Results from a similar study in which chlorinated hydrocarbons (including methylene chloride and methyl chloroform) were introduced into a stainless steel and aluminum chamber having a volume of 600 liters will be discussed (25). The concentration of the chlorinated hydrocarbon was to be approximately its TLV. Welding was then performed by an experienced welder for 15 seconds to 600 seconds on blocks of soft steel. The phosgene concentrations were determined using infrared analysis. Methylene chloride resulted in phosgene concentrations of approximately 1 ppm and methyl chloroform resulted in phosgene concentrations of approximately 0.5 ppm . The author noted that the initial methylene chloride concentration was $730 \mathrm{ppm}(25)$. Unfortunately the authors did not specify precise welding times, but comparison to the two-minute burn time from the current study may be sufficient. In the current study, concentrations of
phosgene produced from methylene chloride and methyl chloroform at their TLV were 3.0 ppm and 5.1 ppm , respectively. These values are three to ten times the values noted earlier for the study discussed above (1 ppm phosgene from methylene chloride and 0.5 ppm phosgene from methyl chloroform). In the current study, heating metals in an atmosphere containing concentrations of methylene chloride and methyl chloroform at one-half the TLV resulted in phosgene concentrations of approximately 0.72 ppm and 1.2 ppm respectively. Values obtained in the current study are again greater (even at the low initial concentration of onehalf the TLV), but comparison is difficult because the difference in initial solvent concentrations.

The phosgene concentrations resulting from the sequence of two-minute burning times for two antispatter compounds that were injected into the chamber by microliter syringes are shown in Table XII. The composition of these antispatter compounds was noted earlier in Table II. One thousand microliters of the antispatter compound were injected into the chamber. Compound A produced 143 ppm methylene chloride and 100 ppm methyl chloroform and Compound B produced 10 ppm methylene chloride and 175 ppm methyl chloroform. Compound A produced much greater concentrations of phosgene than Compound B. This occurrence results from the high concentration of methylene chloride and significant concentration of methyl chloroform produced by the evaporation of Compound A. As noted in the previous
Table XIIPhosgene Concentrations Resulting from the Decompositionof 1000 ul of Antispatter Compound in the Chamber
Cumulative Burn Time (min)

Antispatter Compound A Phosgene Conc (ppm)

Antispatter Compound B Phosgene Conc (ppm)
25.92 .1
4
9.8
4.1
$6 \quad 12.2$
5.15
8
14.2
5.75
10
6.3
12
6.6
experiments, the phosgene concentration increases with increasing burn time, but the rate of phosgene generation decreases with increasing burn time.

The results of spraying the antispatter compound into the chamber and burning the torch for two minutes and then spraying a metal square in the chamber and heating the metal with the torch are shown in Table XIII. Comparison of these results is difficult because there was no measure of the volume of the antispatter compound introduced into the chamber, However, the initial methylene chloride or methyl chloroform concentrations were noted. It appears that heating the metal had no effect, as noted earlier. The values for Compound B are less than those for Compound A, but this may be the result of initially spraying a smaller volume of the antispatter compound into the chamber. However, it may be possible that Compound $B$ does produce $a$ lower concentration of phosgene. Although heating various metals did not affect the phosgene concentrations produced during the decomposition of methylene chloride or methyl chloroform in this study, other studies have identified differences for various metals. In one study in which welding was performed in air containing the vapor of stabilized methyl chloroform, the rate of phosgene formation was greatest for aluminum, then stainless steel, and then carbon steel (12). Results from another study revealed that considerable amounts of phosgene were produced when methyl chloroform was passed over heated iron, steel, or copper

Table XIII
Phosgene Concentrations: Antispatter Compounds Sprayed into Chamber

|  | Antispatter Compound A |  |  |
| :--- | :---: | :---: | :---: |
| Torch <br> Condition | Initial <br> Methylene <br> Chloride <br> Conc (ppm) | Initial <br> Methyl | Chloroform <br> Conc (ppm) |
| In air |  |  | Conc <br> (ppm) |
| On metal | 165 | 135 | 6.3 |
|  | 157 | 125 | 5.1 |

Antispatter Compound B

$$
\begin{aligned}
& \text { Initial } \\
& \text { Methylene } \\
& \text { Chloride } \\
& \text { Conc (ppm) } \\
& \hline
\end{aligned}
$$

In air
15
17

Initial
Methyl Chloroform Conc (ppm)

602
5.4

Phosgene Conc (ppm)
4.8
(10). In the current study, a propane torch was used to initiate the decomposition of chlorinated hydrocarbons. A flame emits very little ultraviolet radiation, but a welding arc emits high intensity ultraviolet radiation. As the welding current increases, the intensity of the ultraviolet radiation increases (11). Ultraviolet radiation is a very effective means of initiating the decomposition of chlorinated hydrocarbons (27). The welding process or the type of metal to be welded may effect the intensity of ultraviolet radiation emitted. Further investigation of this occurrence may provide useful information. A propane torch was used for the current study because it was not practical to weld in the plexiglass chamber. The use of a propane torch instead of welding may explain the differences noted concerning the effect of heating metals on the phosgene concentration.

The Draeger detector tubes were used during these trials to compare their accuracy with the infrared instrument. The infrared instrument measured a phosgene concentration of 12.2 ppm and the Draeger tubes indicated 2.5 ppm . It is difficult to explain such a great difference since the reaction in the detector tubes for phosgene is specific and no other gases have influence on the phosgene indication, according to the literature from Draeger. Furthermore, experimental results confirm that there is no interference from chlorine, hydrogen chloride, and nitrogen dioxide, but the tubes do respond to acetyl chloride (25). Therefore,
the tube readings may be conservative and the actual difference greater. This indicates that the accuracy of the tubes may be questioned and that care must be taken when depending on the tube to evaluate a potentially hazardous environment, and an alternate method may be preferred.
B. Field Study

The results of the field study are shown in Table XIV. The phosgene concentrations recorded in Table XIV are peak concentrations reached during the trial period. The phosgene concentration would peak just following the initiation of welding and stay steady for approximately ten to twenty seconds and then slowly decrease to zero, unless additional antispatter was sprayed during welding. If additional antispatter was applied then the phosgene concentration would peak again. The welding process used for aluminum was not operating properly, so only two values were recorded. A Draeger detector tube was used to obtain the concentration of phosgene present in the welder's breathing zone. The tube indicated a value of 0.5 ppm which correlated closely to a value of 0.4 ppm indicated by the infrared instrument which was slightly closer to the welding surface. Table 14 shows that concentrations above and below the TLV for phosgene ( 0.1 ppm ) were recorded. Variability in phosgene concentrations resulted from the inability to apply consistent volumes of the antispatter compound to the metal surface.

It seems that some manufacturers of antispatter compounds are concerned about the decomposition of chlorinated hydrocarbons in their products. Some labels indicate that the product contains chlorinated hydrocarbons, but not carbon tetrachloride. Other labels indicate that the product contains no chlorinated hydrocarbons. Since

## Table XIV

Phosgene Concentrations: Measured During the Field Study

| Base Metal | Antispatter Compound A |  |  |
| :---: | :---: | :---: | :---: |
|  | $\begin{aligned} & \text { Phosgene } \\ & \text { Conc (ppm) } \\ & \text { Trial } 1 \\ & \hline \end{aligned}$ | Phosgene Conc (ppm) Trial 2 | Phosgene Conc (ppm) Trial 3 |
| Stainless Steel | $<0.1$ | $<0.1$ | 0.15 |
| Mild Steel | 0.2 | 0.5* | 0.2 |
| Aluminum | <0.1 | No data | No data |
|  | Antispatter Compound B |  |  |
| Base <br> Metal | Phosgene Conc (ppm) Txial | Phosgene Conc (ppm) Trial 2 | Phosgene Conc (ppm) Trial 3 |
| Stainless Steel | $<0.1$ | <0.1 | 0.4* |
| Mild Steel | 0.1 | 0.7* | 0.2 |
| Aluminum | <0.1 | No data | No data |

*Detected odor of dichloroacetyl chloride.

Compound B , a newer product than Compound A , contains very little methylene chloride it is possible to surmise that manufacturers may be using methyl chloroform to reduce the health hazards presented by the decomposition products of their antispatter compound. The substitution of methyl chloroform may be based on the stability of methyl chloroform to ultraviolet radiation because of its weak absorption of ultraviolet radiation. One author concluded that methyl chloroform is quite stable to open arc welding energy and phosgene, if generated at all, will be at a low concentration and is not likely to exceed the TLV (24). However, a different author (12) concluded that methyl chloroform is not a safe solvent in the welding environment. This is because methyl chloroform contains stabilizers and their concentration may be greatly reduced over time and therefore the phosgene yield will increase. In addition, the decomposition products from methyl chloroform do not provide any adequate warning properties to indicate the possible presence of phosgene (12). From the results shown in Table XIII and Table XIV it is difficult to identify any differences in the phosgene concentrations generated. Unfortunately it appears that the substitution of methyl chloroform for methylene chloride in antispatter compounds is not effective for reducing the phosgene concentration generated during the decomposition of the antispatter compound.

Since the peak phosgene concentrations generated in the field study were generally low concentrations and the decrease of this peak concentration was quite fast (ten to twenty seconds), it seems that the proper use of antispatter compounds in a well ventilated area would not present an environment that would allow for hazardous concentrations of phosgene. However, the results from the chamber study indicate that high concentrations of phosgene may be produced in some situations. The ventilation in the chamber is not comparable to that found in most welding environments, since there is no air movement through the chamber to allow for dilution of contaminants. The absence of air movement would tend to increase concentrations of the decomposition products in the controlled experimental situation. However, two factors may cause similar concentrations of phosgene to be reached in a practical welding environment. The first factor is the possibility of welding with an antispatter compound in a confined space. The second factor is that the misuse of the antispatter product may result in high phosgene concentrations. Examples of misuse may include spraying large quantities of the antispatter compound and welding before the antispatter dries, spraying the antispatter compound while actually welding, or spraying the antispatter compound every few seconds. Warnings to alert users to such occurrences may be included on labels and also emphasized on Material Safety Data Sheets.

The welder who became ill while using an antispatter compound to provide a smooth welded joint on galvanized steel playground equipment may have been exposed to high concentrations of phosgene. This particular welding environment provided both of the factors that may enhance the development of hazardous concentrations of phosgene. A children's playground tunnel, which may essentially act as a confined space, was being welded together. In addition, the welder was misusing the antispatter compound by liberally applying the compound up to ten times a minute. Therefore, it seems very possible that significant concentrations of phosgene may have been produced. In addition, the burn pattern identified during the biopsy may have been the result of phosgene being carried by the fume (by coating the surface of the fume) to the lower regions of the lung. It is possible that once the fume had become imbedded in the lung tissue the phosgene was hydrolyzed.

## VI. CONCLUSIONS AND RECOMMENDATIONS

A. Conclusions

The information obtained during this study permits the following conclusions:

1. The antispatter compounds contained methylene chloride and methyl chloroform.
2. Concentrations of phosgene created in the experimental chamber setting from the decomposition of methylene chloride or methyl chloroform at one, one-half, and one-tenth of their Threshold Limit Value, were considerably greater than the Threshold Limit Value for phosgene. Therefore the safety of welding in an environment containing methylene chloride or methyl chloroform cannot be determined by the concentration of methylene chloride or methyl chloroform. 3. Heating of one inch square pieces of metal to elevated temperatures in the chamber did not increase the concentrations of phosgene produced. Studies completed by other authors did identify significant variations in phosgene concentrations with different metals. This difference may have resulted from the use of a propane torch which emits very little ultraviolet radiation.
3. Tests of antispatter compounds under actual welding conditions did not produce hazardous concentrations of phosgene under normal conditions.
4. Factors that were identified which may cause hazardous conditions were a confined space or an area with little or no ventilation, or excessive use of the antispatter compound.
5. It is likely that the welder who became ill when using an antispatter compound while welding on children's playground equipment was exposed to high concentrations of phosgene. Exposure may have been intensified because the welder was essentially welding in a confined space and was also misusing the antispatter compound.
B. Recommendations

The following recommendations are made in an attempt to prevent any injury that may result from welders using antispatter compounds:

1. Antispatter compounds that do not contain chlorinated hydrocarbons are available. The use of these products and the development of a variety of such products to meet the welder's needs should be encouraged. Although the use of antispatter compounds containing chlorinated hydrocarbons does not present a hazard in a well-ventilated welding environment, avoidance of any exposure to decomposition products such as phosgene is desirable.
2. To ensure safe conditions in a welding environment which may contain chlorinated hydrocarbons the following measures are recommended. A welding booth should be equipped with both a fresh air intake and an exhaust vent, and should be kept slightly above the pressure of the surroundings to prevent air contaminated with the chlorinated hydrocarbon from getting inside the booth.
3. Welders using antispatter compounds which contain chlorinated hydrocarbons should be warned of the specific hazards and made aware of the precautions to be taken. Labels should clearly identify this information and a Material Safety Data Sheet should also reflect these warnings and precautions. The new Hazard Communication law should improve the content of Material Safety Data Sheets and the information provided to welders.

Current Material Safety Data Sheets for antispatter compounds do not mention the possibility of the formation of hazardous decomposition products such as phosgene. Material Safety Data Sheets for three different antispatter compounds may be found in the Appendix. Another problem concerning the Material Safety Data Sheets is that requests are not always fulfilled.
4. Additional areas to investigate:
a) an in-depth field study at a site where antispatter compounds are used frequently;
b) include in the field study an investigation of the theory that phosgene may be carried to the lower lung region by attaching to the fume and then migrating to the lung tissue where hydrolysis may occur; and
c) also include in the field study an evaluation of the intensity of ultraviolet emissions from various welding processes and various metals. Determine the effect of the intensity of ultraviolet emissions on the phosgene concentrations produced.

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## APPENDIX

## MATERIAL SAPETY DATA SHEETS




| SECTION III . PHYSICAL DATA |  |  |  |
| :---: | :---: | :---: | :---: |
| Berling moint ity |  | yeccific samity iotyor3) | 14 |
|  | 70 max |  | $85=90$ |
|  |  | $\begin{aligned} & \text { EVAMONATION RATE } \\ & \text { I- } \\ & \hline \end{aligned}$ | 1* |
| solvellit in mave * | no |  |  |
| ANPLAMANCE ANO ODOA |  |  |  |





| SECTION VIII - SPECIAL PROTECTION INFORMATION |  |  |  |
| :---: | :---: | :---: | :---: |
| ACShantoav hatection isprofy tomi |  |  |  |
| ventilation |  | Maintain TLV | अनटIAL |
|  | mecteanical IGmend) | Maintain TLV | OTMEA |
| PROTECTIVE GLOVES |  | Maiatala |  |


| SECTION IX - SPECIAL PRECAUTIONS |  |
| :---: | :---: |
| *itcaufions To be tamen in randolina ant Do mot puncture or incine | Keed out of resch of childrep. Do |
| not store at temperatures | $120^{\circ} \mathrm{F}$. Avoid prolonged bresthing |
| OTmEAPAECAUTIONS | of rapors. |

PAGE [2]
$6 * 4=0 \times 50]$

## MATERIAL SAFETY DATA SHEET

Required under USDL Safoty and Health Repulations for Ship Repairing.
'Shipbuilding, and Shipbreaking (29 CFR 1915, 1916, 1917)


SECTION II - HAZARDOUS INGREDIENTS


| SECTION III - PHYSICAL DATA |  |  |  |
| :---: | :---: | :---: | :---: |
| soiling point c $^{9} \mathrm{~F}, \mathrm{~s}$ | 161 | SPECIFIC QRAVITY ( $\left.\mathrm{H}_{2} \mathrm{O}=1\right)$ | 1.5 |
| VAPOR PRESSURE (men Ho.) | U $120 . d \mathrm{H}$ | pelacent volatile ar volutive (s) | 100 |
| VAPOR OENSITY (AIR $=1$ I | -4.55. | EVADORATION RATE <br> ( | 3.5 |
| SOLUBILITY IN WATER | Not |  |  |
| APPEARANCE AND DOOR | COLORLESS TO SLIGHLY AHOCR SOLYFNT OROR |  |  |

## SECTION IV - FIRE AND EXPLOSION HAZARD DATA



## SECTION V - HEALTH HAZARD DATA

```
THAESHOLD LIMIT VALUE FOOPPM
EPFECTS OF OVEREXPOSNDE
    INHALATION: DIZZINESS
    SGLH: DEFATTING, NO ABSORPTION
    HES: LRRLATANT
emCmgenct ano first alo phocegunes
    INHALATION: YENTILATION-FRESH AI合
    SKIN: WASH MITH SOAP AND WATER, APPLY LANOLIM CREAM
    EYEE, FLUSH WTTH WKTER
```

                                    SECTION VI - REACTIVITY DATA
    

## SECTION VII - SPILL OR LEAK PROCEDURES

STEPS TO OE TAKEN IN CASE MATEAIAL IS RELEASEO OA APILLED
MOP, KIPK, SOAK VITH AOSOROEMT MATEDIAL, DISPOSK VIFHIESURFIGIGMT FRESH AIR IN AREA

## WASTE DISPOSAL METHOD

NORHAL IM PLANT

| SECTION VIII - SPECIAL PROTECTION INFORMATION |  |  |  |
| :---: | :---: | :---: | :---: |
| AESPIRATORY PROTECTION (Specily typa) <br> NOMC ESAEMTIAL |  |  |  |
| VWWTILATION | LOCAL EX | 7. | SPECIAL |
| : 'inc | MECHANI | * | OTHER |
| PROTECTIVE GLOVES NOT MEEDED |  | $\begin{aligned} & \text { EVE PROTECTION } \\ & \text { NOT NEEDED } \\ & \hline \end{aligned}$ |  |
| OTHEA PROTEOTIVE EQUIPMENT |  |  |  |

## SECTION IX • SPECIAL PRECAUTIONS

PRECAUTIONS TO RE TAKEN in handlina ano stoaino
STORE YITH RGASQHARLE CARF H COOF PLACE.

OTHER PRECAUTIONS

PAGE (2) COMPILED FROM SOURGES BELIEVED TO BE RELIABLE AND TO FOMT OSMA-ZO REPRESEMT THE BEST CURREMT DPINION. IT SHOULD NOT BE ASSUMEG THA ThEv, MAYTE ADOITIONAL SAFETY MEASURES MAY NOT BE REQUIRED UNDER PARTICULAR OR

## U.S. DEPARTMENT OF LABOR Occupational Safety and Health Administration MATERIAL SAFETY DATA SHEET

Form Aparored OMB No. 44-R13n7

Required under USDL Safety and Health Regulations for 5 hip Repaiting, Shipbuilding, and Shipbreaking (29. CFR 1915, 1916, 1917)


SECTION ॥ - HAZARDOUS INGREDIENTS

| PAINTS, PRESERVATIVES, \& SOLVENTS | \% | $\begin{gathered} \text { TLV } \\ \text { (Unityl } \end{gathered}$ | ALLOYS AND METALLIC COATINGS | $*$ | $\begin{aligned} & \text { TLV } \\ & \text { (Units) } \end{aligned}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| PIGMENTS | NO |  | BASE METAL | NQ |  |
| CATALYST | NO |  | ALLOYS | NO |  |
| VEHICLE NOT LESSTHAN | 1. |  | METALLIC COATINGS | NO |  |
|  | 92 |  | pillea metal PLUS COATINA OR CORE FLUX | NO |  |
| additives base producit (UIL) | 7 |  | OThERS | NO | - |
| OTHERS | NO |  | - |  |  |
| HAZARDOUS MIXTURES OF OTHER LIQUIDS, SOLIDS, OR GASES |  |  |  | x | $\begin{aligned} & \text { TLV } \\ & \text { (Unitu) } \\ & \hline \end{aligned}$ |
| N/A |  |  |  |  |  |
| . |  |  |  |  |  |
| = |  |  |  |  |  |
| $\because$ |  |  |  |  |  |


| SECTION III - PHYSICAL DATA |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: |
| BOILING POINT ( ${ }^{\circ} \mathrm{F}$.) | 4 | 165 | SPECIFIC GRAVITY ( $\left.\mathrm{H}_{2} \mathrm{O} * 1\right)$ | 1.30 |
| VAPOR PRESSURE (mm Hel) | - | i. 120.5 | PEACENT, VOLATILE No VOLUME ( N ) | Not KNOH |
| VAPOA DENSITY (AIR=1) |  | 4.55 | $\begin{aligned} & \text { EVAPORATION RATE } \\ & \left(\begin{array}{l} \text { (1) } \\ \hline \end{array}\right. \end{aligned}$ | 3.50 H |
| SOLUBILITY IN WATEA |  | No |  |  |
| apprarance ano ocon CoLORLESS, SOLVENT ODOR |  |  |  |  |

SECTION IV - FIRE AND EXPLOSION HAZARD DATA

|  | FLammagle limits | L* 1 | Ue1 |
| :---: | :---: | :---: | :---: |
| EXTINGUISMING MEDIA NOT NEEDED |  |  |  |
| SPECIAL FIRE FIGHTING PROCEDURES |  |  |  |
|  |  |  |  |
| UNUSUAL FIRE ANOEXPLOSGN HAZARSOL CAN |  |  |  |
|  | 1 |  |  |

## SECTION V • HEALTH HAZARD DATA

```
THRESHOLD LIMIT VALUE
    550 PPM
CMFECTS OR OVEREXPOSURE'\
    DEFATTING SKIN, INGESTION-VERY LOW TOXICITY
EMEAGENCY ANO FIRST AIO PROCEOURES
    INHALAT ION-REMOVE TO FRESH AIR
    SKIN - WASH SOAP AND WATER, EYES- FLUSH WITH WATER,
    INGESTION-TREAT SYMPTOMATICALLY
```



## SECTION VII - SPILL OR LEAK PROCEDURES

```
STLM, TO be TAKEN IN CASE MATERIAL IS RELEASEO OR SPILLEO
    ALLOW TO EVAPORATE OR MOP, WIPELWITM. ASORPENT MATSRIAL
    DISPOSE IN NORMAL PLANT PROCEDURES. AREA SHOULD HAYE VENTILATION
```



| SECTION VIII - SPECIAL PROTECTION INFORMATION -- |  |  |  |
| :---: | :---: | :---: | :---: |
|  |  |  | ${ }^{\text {SPECLIAL }}$ |
|  |  |  |  |
| NORMAL IN MEANANICAL (Gememal) |  |  | OTHEA |
|  |  | Eveprotection |  |
| OTHER PROTLCTIVE EQUUPMENTNOT NEEDED |  |  |  |

## SECTION IX - SPECIAL PRECAUTIONS



OTHER PRECAUTIONS

PAGE (2)
CONPILED FROM SOURCES BELIEVED TO BE RELIABLE AND TO REPREGEXEHACOMO ARE BEST CURRENT OPINION. IT SKOULD NOT BE ASSUMED THAT MEV, MEY 72 ADDITIONAL SAFETY MEASURES MAY NOT BE REQUIRED UNDER PARTICULAR OF EXCEPTIONAL CONDITIONS OF USE.

