OPPORTUNITY FOR RISK REDUCTION AND INNOVATION

Engineering Opportunities

Occupational exposures are currently being managed through the use of various control technologies. The most effective means are engineering controls, particularly high volume low pressure spray guns and downdraft spray paint booths. Other controls such as personal protective equipment including respiratory protection are also being used.

High Volume Low Pressure (HVLP) spray guns are the most effective spray guns at controlling occupational exposures. This is because they are better at atomizing the air stream resulting in a more controlled spray pattern, less bounce back, and enhanced transfer efficiency. In addition, they have a higher transfer rate than other types of spray guns (Heitbrink, 1995). As a result, HVLP technology has become commonplace in the industry (BAAWMD, 1995). As stated earlier, in 1995, approximately 64% of U.S. auto body shops reported owning HVLP equipment (approximately 49% of small auto body shops (<$124,999 annual sales) and approximately 68% of very large (>$1 million annual sales). Also in 1995, approximately 12% of auto body shops surveyed planned to purchase HVLP spray equipment (BSB, 1995). This provides an opportunity to encourage the wider use of HVLP spray guns and in providing product stewardship information to help counter some of the perceived disadvantages.

The wider adoption of spray booths provide the opportunity to reduce general worker exposure. The types of booths include both downdraft with either dry-type when painting is limited or waterfall or cascade scrubbers when high volume spray coating operations are conducted for several hours a day. For example, NIOSH recommendations in their Hazard Control documents that "properly used and maintained HVLP spray painting guns and downdraft booths will greatly reduce paint overspray concentrations, but they will not completely eliminate overspray from the air that workers breathe. Therefore, Personal Protective Equipment is also recommended with a Respiratory Protection Program that contains all of the elements currently required by the OSHA standard (such as worker evaluation, selection of appropriate air purifying or supplied air respirators, fit testing, training, and maintenance needed to fully protect workers from this hazard." (NIOSH, 1996)

Green Chemistry Opportunities

The Pollution Prevention Act of 1990 (PPA) establishes a national pollution prevention ethic in dealing with environmental problems in the United States. The PPA states that:

> "The Congress hereby declares it to be the national policy of the United States that pollution should be prevented or reduced at the source whenever feasible; pollution that cannot be prevented should be recycled in an environmentally safe manner, whenever feasible; pollution that cannot be prevented or recycled should be treated in an environmentally safe manner whenever feasible; and disposal or other release

into the environment should be employed only as a last resort and should be conducted in an environmentally safe manner."

During the past several years, the chemical industry has put a lot of efforts toward pollution prevention issues associated with the manufacture and use of various chemicals. Particularly, in the PPA's mandate on source reduction. Source reduction in the PPA is defined, in part, as

"any practice which (I) reduces the amount of any hazardous substance, pollutant, or contaminant entering any waste stream or otherwise released into the environment (including fugitive emissions) prior to recycling, treatment, or disposal; and (ii) reduces the hazards to public health and the environment associated with the release of such substances, pollutants, or contaminants."

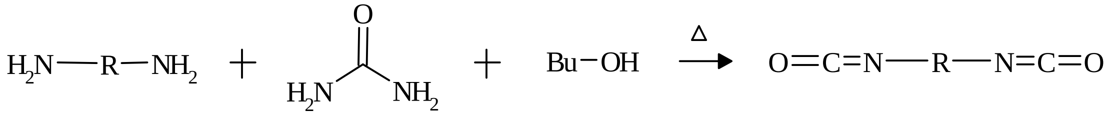
A great number of innovative chemistries (e.g., Green Chemistry practices) have been developed under this mandate.

Practices in Isocyanates Manufacture

Isocyanates monomers are commonly produced by the phosgenation processes as mentioned before. In the present day climate of moving toward greater protection of health, safety, and the environment, efforts to replace phosgene with safer substitutes that by design are benign chemical processes are gaining ground. Some examples of new phosgene-free synthetic pathways have been identified. They show potential for replacement of conventional phosgenation processes long used by the isocyanates chemical industry.

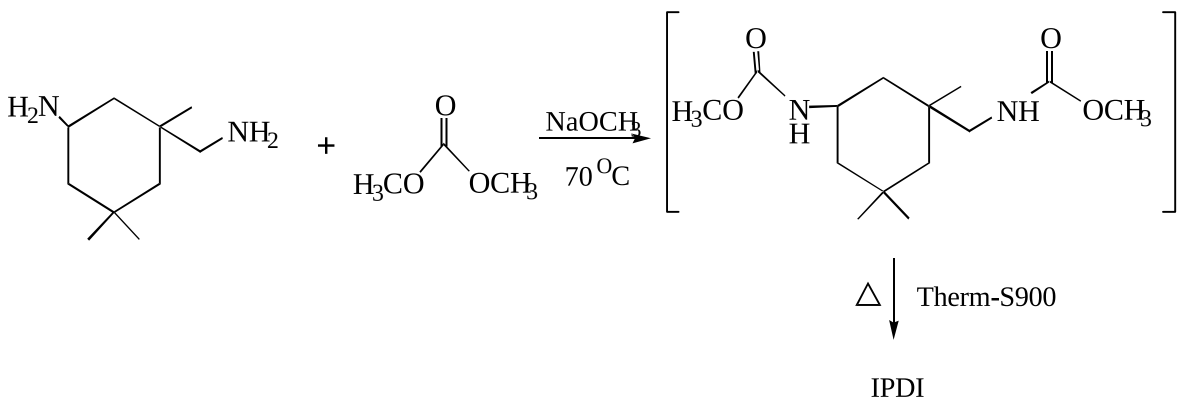
<u>Huls A.-G.'s Urea Adduct-based, Phosgene-free Diisocyanate Process</u>

During the past ten years Huls in Germany has developed a novel, pilot-scale process for the production of diisocyanates from diamines. The new route accomplishes the conversion of isophorone diamine (IPDA) to IPDI using a urea adduct-based process. Huls has announced this will be the large scale manufacturing process used in the $40 million diisocyanate plant to be operational in Theodore, Alabama, by 1996. According to Hunter and Rotman, it is said to be a highly versatile technology by which "any diamine can be converted [into a diisocyanate]" (1994). Hul also manufactures other aliphatic diisocyanate raw materials for the coatings industry that are said to include the saturated compounds, dimethyl diisocyanate and hexamethylene diisocyanate. BASF A.-G. (Germany) has a similar process developed to produce various diisocyanates (Hellbach *et al*, 1984; Merger *et al*, 1984). The overall reaction is:



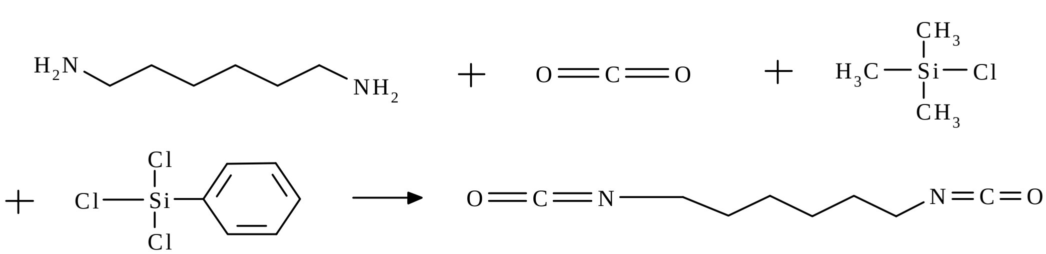
<u>Daicel's Phosgene-free Process to Produce Diisocyanates via Diurethanes</u>

Daicel Chemical Industries, Ltd., has patented a process for reacting diamines such as isophorone diamine (IPDA) with dimethyl carbonate (Yagii *et al*., 1988). The condensation is accomplished in the presence of an alkaline catalyst such as methanolic sodium methylate at 70º C to produce the diurethane. Treatment of the diurethane with hydrogenated terphenyl containing manganese acetate at 230ºC in vacuo produces isophorone diisocyanate by thermal decomposition. This non-phosgene process has a reported product yield of 93% of IPDI containing 1% isophorone monoisocyanate. The overall reaction is:



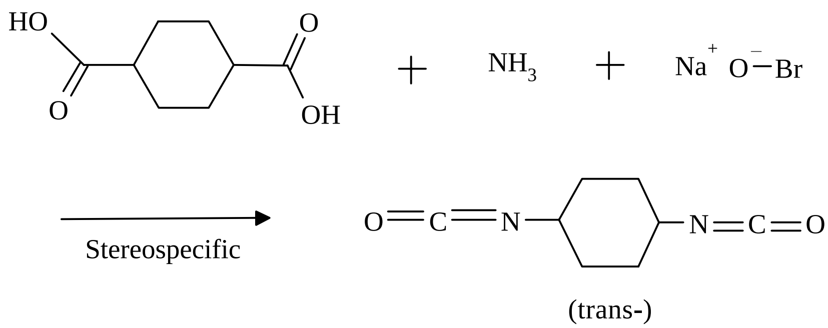
<u>Union Carbide Corp. - CO_2- based Process to Produce Diisocyanates</u>

This process offers an alternative for isocyanates from amine and dry ice via halosilyl carbamates intermediate without using phosgene. The silylcarbamate was trans-silylated with trichlorophenylsilane and then heated to give hexamethylene diisocyanate (Hedaya et. al., 1981). The reaction is:



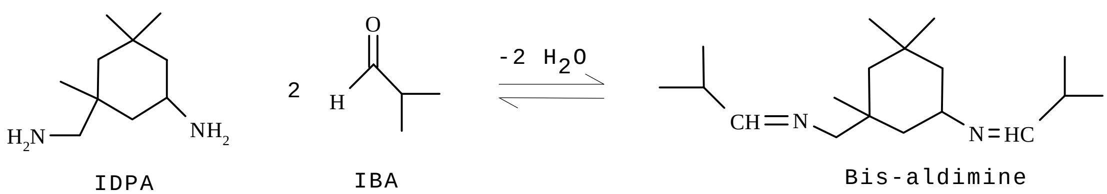
<u>Akzo Corp., Obernburg (Germany) - Phosgene-free Process to Produce Diisocyanate</u>

This is a new phosgene-free process for isocyanates/diisocyanates from acids or esters (Zengel *et al*, 1980). Terephthalic acid or 1,4-cyclohexanedicarboxylic acid (obtained from hydrogenation of terephthalic acid) were converted to diisocyanate by a 4-step process consisting of ammonolysis, amide chlorination (or bromination), Hofmann rearrangement, followed by ureathane cleavage (if $Br_2/NaOCH_3/CH_3OH$ were used in Hofmann rearrangement). The reaction is as follows:

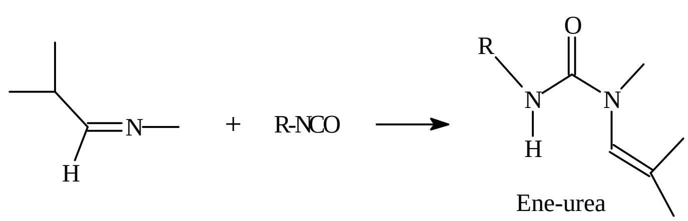


Practice in Other Area

Under the President's Green Chemistry Challenge Awards Program for 1995-1996, Bayer Corporation submitted a nomination, titled "A Foundation for Environmentally-Friendly High Solids Coatings"(Bayer Corp., 1995). The technology presented is a reactive coating system comprised of an aliphatic polyisocyanate and a low viscosity, bis-aldimine functional resin. The bis-aldimine resin is formed by the reaction:



The bis-aldimine resin has viscosity of less than 100 mPa. Therefore, it also functions as solvent in the coatings/paints application to reduce the VOC content. When this bis-aldimine reacts with isocyanate, it gives an Ene-urea without releasing aldehyde (scheme below). Water is the catalyst for isocyanate reaction.



Environmental Benefits of the Technology

VOC Reduction in Polyurethane Paints

The aldimine coreactants were developed with the intention of reducing the VOC content of 2-component polyurethane coatings. Due to the lower viscosity of the aldimines as compared to traditional products, a smaller amount of solvent is required to get the coating material to the desired application viscosity.

Waste Reduction

When aldimines are mixed with polyisocyanates, the formulations increase very slowly in viscosity as long as they are stored in a closed container. The paint therefore has a long pot life, thus minimizing the amount of unused paint which must be disposed. In addition, in contrast to typical high-solids coreactants, the paint dries quickly at ambient temperatures after its application, and thus avoids the time and energy requirements for thermal baking of the coating.

Control of Release into Aqueous Environments

The parent amines used for the aldimines are water soluble but the aldimine products themselves are characterized by very low solubility. According to Bayer's document, there is no hydrolysis of aldimines (detectable by IR) when they were exposed to a large molar excess of water, even when the reaction is run homogeneously in a polar organic solvent. This insolubility provides two major benefits. First, it aids in the physical isolation of the product in the case of release. Second, it keeps the product available for reaction with the polyisocyanate which is also insoluble in water.