INDUSTRIAL CHEMICAL SAFETY AND VINYL CHLORIDE

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Vinyl chloride plastics are among the oldest of the major plastic materials. The first commercial PVC resin plants were constructed in the 1930s and initially produced only rubbery products. Today about two-thirds of the PVC products are still rubbery in nature, but the balance is made into rigid

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articles such as pipe, siding, and phonograph records. A unique property of PVC resin is one which permits it to be combined with many other raw materials to form a myriad of different compounds with wide variations in properties. This characteristic along with its flame resistance and low cost have resulted in PVC being one of the most important plastics in existence today throughout the world.

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The quantity of VCM produced globablly has grown to 24 billion pounds with a U.S. production of 6 billion pounds.

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There are two commercial routes to vinyl chloride: the addition of hydrogen chloride to acetylene and thermal cracking of ethylene dichloride. The latter is the principal process used by Dow and most other U.S. producers. Vinyl chloride is one of the purest organic compounds produced commercially. A typical analysis of VCM produced will show less than 20 ppm total organic impurities.

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Vinyl chloride has received a great deal of publicity in the past few years as a human carcinogen, specifically a cause of angiosarcoma, a rare liver cancer.

It seems worthwhile to follow a brief chronology of the recognized health hazards of VCM. In the 1930s the chief concern for worker safety was from fire or explosion of VCM and all precautions were aimed at this recognized hazard. By 1954 VCM was recognized as a mild anesthetic. A level of 500 ppm was recommended as a maximum average exposure. In 1961 Dow reported that 4-1/2 to 6 months exposure of animals to levels down to 100 ppm for typical work weeks resulted in slight liver damage. Because of this, Dow recommended that 50 ppm be the average exposure level with an excursion limit of 100 ppm. However, in 1962 Yale workers claimed 500 ppm was safe based on their own studies.

In 1970 Viola reported that rats exposed to 30,000 ppm of VCM for one year showed skeletal damage (acroosteolysis like) and later tumors. The details of this work were not published until the following year.

In 1971, OSHA established 500 ppm VCM as a national standard.

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By 1972, the situation was becoming more confusing, particularly because of rumors coming from Maltoni's laboratories; so, 17 U.S. companies agreed to support VCM animal studies to establish true safe levels. Human epidemiological studies were also started.

In 1974 the angiosarcoma deaths of several workers were announced by U.S. industry. As a result OSHA set an emergency temporary standard of 50 ppm and set 1 ppm as the allowable plant level long term. The 1 ppm standard is the current law with a temporary 25 ppm level during a one year adjustment period. This year the FDA and EPA became quite active in generating and obtaining data for food and emission standards.

In 1976 the 1 ppm standard will come into effect. What is the basis for all of this flurry of activity? A very low "safe" level has been chosen because we have had no "exact" data to support a higher level.

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In seeking a safe level of exposure to vinyl chloride, we have a lot of theory but less solid information at this time. It is obvious that the workers who developed angiosarcoma were generally exposed to very high concentrations, probably in the range of thousands of parts per million. Animals exposed to 50 ppm have developed tumors. Exposures to lower concentrations have not been completed at this time.

It appears to be necessary to metabolize VC before it becomes carcinogenic. Animal studies indicate that metabolism changes as the exposure concentrations decrease to about 50 ppm. Animal metabolism studies have shown that in this range inhaled VCM is not bound to the liver protein, and the metabolites are detoxified. Above levels of 50 ppm the biological defense system may be over-ridden and the VCM metabolites are not all detoxified. At these levels, the damage is done.

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Oxidation products are metabolites of VCM exposure.

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Most toxicologists consider that all substances have a dose response level for acute effects and chronic effects. Alcohol is the most familiar case. We all know that alcohol will produce death both from its acute and chronic effects if exposure is high enough. On the other hand, low levels can be tolerated with no ill effects for years.

Thus, legal safe levels of exposure to chemicals should be based on experimentally obtained data to put the control in proper perspective.

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Given that we are at 1 ppm - How do we comply with the law and protect our workers?

By lowering plant levels through engineering and control. Some jobs such as maintenance and tank car loading may always need protective gear. Plant monitoring is another tool. Respiratory gear and protective clothing are also methods in use.
Let's consider some of this equipment.

Slide 11 (5)

This particular panel contains flammable gas detector alarms for strategically placed sensors to detect major leaks or spills. The trend is towards huge single train units rather than several smaller units, which greatly reduces the chances for emissions.

Slide 12 (11)

In addition to engineering, good work place monitoring is essential such as spot sampling with gas bags and continuous

Slide 13 (12)

charcoal absorption. The carbon disulfide desorbed

Slide 14 (13)

sample is being analyzed here by gas chromatography.

Slide 15 (14)

Area monitoring has also helped identify problem places such as tank car loading stations.

Slide 16 (15)

The level in the tank car has been determined by gas escaping from this tube. The

Slide 17 (16)

operator is wearing a face mask breathing device to avoid exposure to the gas.

Slide 18 (18)

The trend is towards monitoring car loading by magnetic gauges, even though heat sensing devices such as this have been successful. Line disconnecting has been another problem

Slide 19 (19)

area that

Slide 20 (20)

is being corrected by purge lines.

Slide 21 (21)

On stream sampling devices are being developed to minimize line opening for analysis.

Slide 22 (22)

This operator is taking a typical grab sample while using a mouth respirator.

Slide 23 (23)

This closed system of taking samples gives much less chance for emissions.

Slide 24 (24)

Analysis is being done in a hood.

Slide 25 (25)

A sample from a close bottle is being put into a flask in the hood.

Slide 26 (26)

Another closed sample station.

Slide 27 (27)

Carcinogen warning sign at Dow Saran Resin Plant.

Slide 28 (38)

Extensive on-line instrumentation is used in the resin plant to minimize opening lines. Note the continuous area pick-up probe on the wall.

Slide 29 (40)

This is an on-line resin sampling device.

Slide 30 (41)

Provision is made here to drain lines and purge before opening to the atmosphere.

Slide 31 (2-1)

Personal protective equipment is important for plant safety and we will consider some respiratory equipment we have in use.

Slide 32 (2-2)

This is an ACME cartridge type which is quite handy. It was tested to breakthrough and lasted 15 minutes.

Slide 33 (2-4)

This is a larger cartridge ACME.

Slide 34 (2-5)

It lasted 22 minutes.

Slide 35 (2-6)

A less convenient but longer lasting

Slide 36 (2-7)

cannister type.

Slide 37 (2-8)

Of interest here is data comparing two charcoals. Breakthrough to 1 ppm was in 75 minutes with Calgon PCB 12x30, while supplied AOR-31 was at 35 minutes (flow rates are 32 l/min).

Slide 38 (2-9)

Better, but less handy is this air hood.

Slide 39 (2-11)

This continuous air flow full face mask is probably the best of the air supplied breathing apparatus, but it still has the hose restriction.

Slide 40 (2-12)

For air flow plus mobility, this tank type face breathing gear is good, but limited to about 15 to 30 minutes.

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The type of breathing apparatus used is dictated by the situation.

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To avoid skin absorption, protective clothing must be used.

Slide 43 (2-16)

This fully pressurized suit with self-contained breathing air will give complete protection but has its disadvantages.

Slide 44 (2-17)

In our Texas Division the following test was run. The beginning body temperature was 98.4°F. After sitting five minutes skin temperature was 100.9°F.

Slide 45 (2-18)

After five minutes of walking body temperature was 102.6°F and skin temp was 101.8°F. Ambient temp was 85°F. Obviously this type of suit can only be worn under certain conditions.

This has been a rather broad overview of vinyl chloride history, size, government regulation, toxicity, and safety equipment. Time does not allow detail, but I will be glad to answer any questions you may have.