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IMPERIAL CHEMICAL INDUSTRIES LIMITED
PLASTICS DIVISION

TALK TO BE GIVEN AT RAPRA ON 8 MARCH 1978 TO SOCIETY OF ENVIRONMENTAL ENGINEERS

CONTROLLING VINYL CHLORIDE MONOMER (VCM)

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1 Objective of Paper

In this paper it is my aim to give you an insight into what happened when in 1974 the PVC industry found itself faced with an unsuspected health hazard, how the hazard was assessed and controlled and also how regulations have been and still are being promulgated in various countries. In particular I should like to discuss the problems of harmonisation of regulations in the EEC. This will not be a treatise on analytical and monitoring methods which have recently been described in great detail by my industry colleagues at the International Conference on "The Monitoring of Hazardous Gases in the Working Environment" at The City University, 12-14 December 1977 and the SIRA Conference on "Monitoring Toxic Hazards" 27-28 September 1977 at the Cutlers Hall in Sheffield. These methods have also been given exhaustive treatment in the CIA Plant Manual "The Determination of Vinyl Chloride", now in its 3rd edition in as many years. Towards the end of 1978 it is hoped that IARC will issue a monograph on "VCM Analysis" written by W Thain of BP and D C M Squirrell of ICI. There is an abundance of information already printed or about to be printed which will illustrate the first class job done by British analysts and instrument engineers in developing the methods and hardware to monitor and control VCM exposures.

2 Background Information

(a) VCM and PVC in Europe

Vinyl chloride monomer (VCM) or monochlorethene $\text{CH}_2 = \text{CHCl}$ was described by Regnault in 1835. Though work was done on polymerising VCM to polyvinyl chloride (PVC) as a rubber substitute principally in Germany in World War I, the real growth in manufacture and use of VCM did not start until the 1930's when techniques were devised to polymerise VCM into stable forms of PVC which could be compounded and fabricated economically. Bulk manufacture of VCM and PVC has a 45 year history and world consumption has now reached 10 million tonnes pa which puts PVC in the top three plastic products polyethylene, PVC and polystyrene.

The principal use of VCM is in the manufacture of PVC. About 30 European companies make 3.5-4.0 m tpa of PVC at 50 factory sites. The market is broadly based. It is also well spread over the populations of Europe;

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some selected European consumption per head figures are interesting in comparison with figures from countries outside Europe. (Table 1)

Table 1. Selected consumption per head of PVC in some countries in and outside Europe

	1974 (kg/head of population)
West Germany	15.2
France	12.1
UK	7.3
Japan	11.4
USA	9.5
Canada	6.1

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The average per caput consumption in Western Europe exceeds 10 kg; PVC occupies an important place in the plastics industry in Europe.

In Western Europe with roughly $\frac{1}{3}$ of the world consumption of PVC, 10,000 people are employed in the manufacture of VCM and PVC and it is estimated some 350,000 people in PVC fabrication. The sales turnover of the PVC polymer industry in Europe is about \$2 billion. Sales of fabricated products must be much higher in value, perhaps by a factor of 2 to 3 times.

2(b) Outline of PVC Manufacture

Since VCM has a boiling point of -13.5°C and is polymerised at $40-70^{\circ}\text{C}$, the polymerisation process must be carried out under pressure in an autoclave. Because the reaction is exothermic, means of heat removal must be found to control the reaction. This control is most usually achieved by dispersing the liquid monomer into tiny droplets ($100\mu\text{m}$ in diameter) in an equal weight of water. As polymerisation proceeds, a 3 phase system of solid polymer precipitates within liquid monomer droplets which are in turn dispersed in a continuous water phase. Though much research has been devoted over the past 30 years to the stabilisation of this system, a continuous film of PVC builds up on the inner surface of the autoclave and if this is not removed, the heat transfer

characteristics of the vessel are impaired. Inability to prevent this build-up is one of the basic reasons why the polymerisation process is essentially batch. The need for manual cleaning of these autoclaves in the past proved to be a key element in the consideration of health hazards.

At 95% conversion, the reaction becomes uneconomically slow. At the termination point of the reaction, the 5% residual VCM at a pressure of 4-5 atmospheres is vented back to a gasholder and a slurry of PVC particles (100-150 μm in diameter) suspended in water left in the reactor. Since VCM has a strong affinity for PVC, the last traces of VCM are difficult to remove from the polymer. The slurry after stripping contains 500 ppm of VCM. The slurry is centrifuged and the powder dried. The dried powder which can contain up to 50 ppm of VCM is sold in bulk containers or in bags. At the next stage before fabrication, the powder is mixed with fillers, plasticisers, stabilisers, etc; there is a further loss of residual VCM at this stage. There is very little if any loss during the fabrication operation.

To re-start the cycle in this process, the empty autoclave which still contains VCM gas is further evacuated and purged before being opened to the atmosphere and automatic high pressure water jets are activated to remove polymer scale from the walls. To give some idea of size, the autoclaves range in volume from about 5 m^3 to 200 m^3 with the majority in the range 10 m^3 - 80 m^3 . A typical charge for a 10 m^3 autoclave would be 4 tonnes of VCM.

2(c) The Toxicology of VCM

In the 1930's VCM was investigated as an anaesthetic but judged to be unsatisfactory because of its circulatory and cardiac effects at 10-20% volume, a dosage not significant for industrial exposure where one has to operate at less than the 4% by volume in air lower explosive limit. VCM at 2.1% by volume or 25,000 ppm in air will cause dizziness and disorientation in man in 3 minutes. At 6,600 ppm dizziness and sleepiness are experienced in 30 minutes. Odour is detectable at 4,000 ppm. VCM was considered to be a material of relatively low toxicity and the American Conference of Governmental Industrial Hygienists (ACGIH) in 1959 recommended a TLV of 500 ppm for exposures of 8 hr TWA. Manufacturers saw the main hazards associated with VCM to be fire, explosion and narcosis.

Though some animal experiments by Dow in 1961 led to a querying of the 500 ppm TLV and suggestions that 100 ppm might be more appropriate, no serious doubts about the long term toxicity of VCM emerged until the mid 1960's when it was found that a few autoclave cleaners developed acro-osteolysis (AOL), a condition affecting the terminal bones of the fingers. In addition soft tissue changes, coldness and numbness of the hands and finger tips similar to Raynaud's phenomenon were observed. These symptoms were found in men who went inside the autoclaves to scrape and clean the PVC film off the walls between polymerisation cycles. Though methods of controlling and improving this situation were devised the European PVC producers were left extremely worried about this unexpected development. Professor Viola of Solvay in Italy tried to reproduce AOL in animals by exposing them to 30,000 ppm of VCM.

Professor Viola could not reproduce the AOL condition but he did find he produced tumours in experimental animals. A group of European manufacturers (Solvay, Rhone-Poulenc, Montedison and ICI) decided therefore to sponsor work with Professor Cesare Maltoni (Institute of Oncology, Bologna, Italy) who exposed rats to inhalation experiments for 12 months, 5 days/week, 4 hours/day to concentrations of VCM ranging from 10,000 ppm to 50 ppm. At all dose levels, Professor Maltoni found a considerable yield of tumours of many types in glands and liver but predominantly the rare tumour, liver angiosarcoma.

As soon as Professor Maltoni reported this work to the European sponsoring group, his findings were communicated to PVC producers elsewhere in the world. Epidemiological studies were undertaken both in Europe and the USA. The first positive results were obtained in the USA where in late 1973/early 1974 BF Goodrich found deaths due to the rare liver cancer, angiosarcoma, in three men who had previously been autoclave cleaners. Soon evidence of angiosarcoma deaths also became apparent in the European mortality studies. It was clear from these deaths above the normal expected rate and other accumulating data, that VCM was a human carcinogen. For the first time in its history, the plastics industry was facing a health hazard of major concern.

3 Assessment of the Health Hazard

The word "cancer" is highly emotive and the linking of "cancer" with exposure to an industrial chemical made on a 10 m tpa scale caused genuine alarm in 1974. To eliminate the risk completely would have entailed the complete shutdown of the industry which would have had far-reaching social and economic consequences. Industries dependent on supplies of PVC range from building to coal mining, motor vehicle production, electrical goods, electricity supply,

footwear, food packaging, etc, etc. While the possibility of substitution by other materials exists, in many outlets PVC has found its place by virtue of properties such as oxygen permeability, toughness, self-extinguishing in fire situations, flexibility, etc and the balance of properties/economics make it difficult to replace except at great cost and perhaps also at the expense of other health and safety risks.

Shutdown was in fact seriously contemplated and a small number of plants did close temporarily and a few permanently. In general however all over the World the pattern was the same. Governments, manufacturers and unions reviewed the problem and concluded that under certain conditions the danger could be contained. A hierarchy of health hazards was assessed as follows on the basis that health problems with VCM were associated with long exposure (20 yrs average) to high concentrations of VCM (hundreds of ppm average with peaks in thousands of ppm).

- (a) The greatest hazard was in VCM polymerisation plants where atmospheric concentrations 20 years ago might have reached $>1,000$ ppm at times and where, with reductions during the years, levels averaged around 150 ppm by 1973.
- (b) The second highest hazard was in VCM production plants with average area concentrations of perhaps 5 ppm though there had been high peak concentrations in early days of manufacture.
- (c) The third highest hazard was in PVC fabrication plants with average levels of 2 ppm though again in the past or in conditions of poor ventilation the concentration could have risen to say 50 ppm.
- (d) Fourth in rank was the environment at factory boundaries where concentrations in 1974 were 0.1 ppm and below.
- (e) Fifth in rank were foodstuffs and beverages. VCM traces remain in bottles and food wraps and as a result parts per billion of VCM can be found in the food product.

4 Reducing and Controlling the Hazard

Hygiene has been improved considerably all round by reduction in exposure of all personnel in VCM, PVC, fabrication works, etc. Some of the improvements have been obtained as follows:-

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- (a) the autoclave cleaning job has been substantially altered and the aim is to eliminate it completely;
- (b) equipment and manufacturing methods have been modified so that the average "area concentrations" of VCM in most plants is in the 1-5 ppm range though local excursions are experienced from time to time when leaks occur;
- (c) improved ventilation, the availability of "safe refuges" and the wearing of breathing apparatus at certain alarm levels have resulted in "personal exposures" lower than measured "area concentrations";
- (d) analytical methods and equipment have been developed to test area concentrations at frequent intervals and give alarms at appropriate levels; if anything we now suffer from a surfeit of analyses (eg 10,000 per plant per week);
- (e) residual VCM is being removed much more efficiently from polymer and recovered; if the polymer is mixed or compounded efficiently with fillers, etc. as recommended by BPF and the manufacturers, there is very little, if any, further loss during subsequent fabrication processes;
- (f) pumps, pipelines, valves, etc. are the subject of special care to reduce leaks;
- (g) stripping, recovering and venting have been modified so that VCM concentrations at factory boundaries are now very low, many of the measurements being less than 0.01 ppm.

It is interesting to note in the following table 2, the drop achieved in average exposures.

Table 2. Historical VCM exposures (estimated)

1945-1955	1,000 ppm
1955-1960	400-500
1960-1970	300-400
Mid 1973	150
1975	5

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Post 1975, much depends on plant, process and perhaps most important of all method of measurement and calculation. By and large I would say that most VCM plants are below 1 ppm and most PVC plants in the range 1-5 ppm. Well ventilated PVC fabrication plants by and large are all below 1 ppm. Factory boundary readings have been variously reported but where they are detectable they are around 0.01 ppm.

The capital cost to date of these improvements in the UK in the past 4 years have been £15m; this does not include research costs, loss of revenue during production interruptions etc which were considerable. On a pro rata basis world capital expenditure would have been at least £300m. This expenditure continues to grow but at a diminishing rate since diminishing returns for the effort expended are now being experienced. Research into improved processes, methods and products continues urgently. Now that the industry is aware of the hazard, new plants are being designed ab initio to give better control of hygiene.

5 Extent of the Health Problem

In the UK there have been 5 cases of AOL which is non-fatal and in part reversible. In Europe there have been about 40 AOL cases and in the USA around 25, all autoclave cleaners. We believe AOL cases are a thing of the past.

There have been about 70 ASL (angiosarcoma of the liver) cases in the World to date. The distribution of these ASL cases is interesting.

Table 3. Pattern of ASL cases

Germany	10	USA	23
France	10	Canada	10
Sweden	4		
Italy	2	N America	33
UK	2		
Norway	1	Japan	2
Belgium	1	Yugoslavia	2
		Czechoslovakia	2
W Europe	30		

ie W Europe 30
 N America 33
 Rest of World 6
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Of the 30 ASL cases in W Europe, 19 have occurred in clusters of 2, 3 and 4 at 6 plants. There are 50 plants in Europe and of these 32 have not had any ASL cases. Of the 33 ASL cases in North America, 28 have occurred in clusters of 3, 5 and 2 x 10 in 4 plants out of a total of 53 plants - in North America 45 plants have had no ASL cases.

6 Worker Hygiene Regulation

To regulate worker hygiene, various measures were adopted in different countries.

Table 4. Regulations to protect VCM exposed workers

	<u>Average Exposure Limit</u>
W Germany	5 ppm (1 year average) for existing factories 2 ppm (1 year average) for new factories and also for PVC fabricators
Belgium	5 ppm (1 week average)
Denmark	1 ppm (8 hour average) <u>for PVC fabricators - personal</u>
Finland	5 ppm (8 hour average) - <u>personal</u>
UK	10 ppm (8 hour average)
Sweden	1 ppm (8 hour average) - <u>personal</u>
Switzerland	10 ppm (1 week average) - <u>personal</u>
USA	1 ppm (8 hour average) - <u>personal</u>
Proposed EEC	3 ppm (1 year average) for VCM and PVC factories

This is a much simplified table and does not include details of alarm levels and maximum exposure levels which vary from country to country.

Regrettably our medical and biochemical indicators are so imprecise at our present state of knowledge that the sort of spread displayed in Table 4 is inevitable. The figures have been variously reached by the exercise of judgement as to what was practicable and reasonable, by negotiation or by court action. Everyone agrees that worker exposure to VCM should be minimised and reduced as close as possible to zero.

The figures given above immediately display the problems of measuring and monitoring human exposure on any comparable basis. In the absence of reliable individual monitoring devices which can give immediate alarm signals when leaks or higher than normal readings occur, one has to depend on work area measurements and scanning work areas sequentially to get a large number of readings from which one can derive Time Weighted Average (TWA) exposures and at the same time give prompt alarms for protective measures to be taken.

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The TWA exposures as you will see vary from periods of 8 hours to 1 year. As you are well aware these are very different figures for different time weightings. The coefficients for conversion from one period to another are contained in Table 5.

Table 5

<u>Reference Period</u>	<u>Conversion Coefficient</u>
1 year	1
1 month	1.7
1 week	1.95
8 hours	2.3
1 hour	2.55

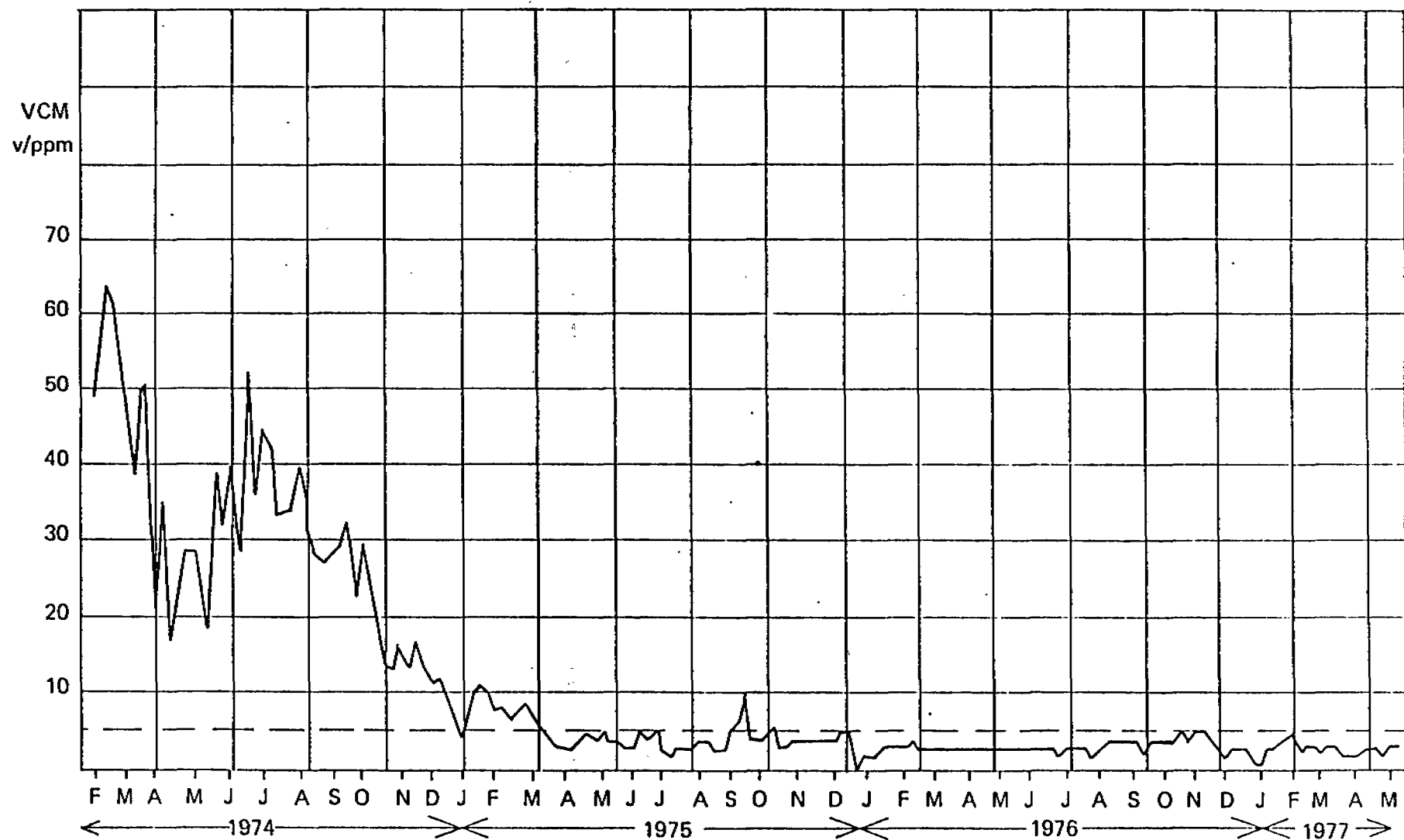
Translated into the more familiar 8 hour TWA, Table 4 has been re-calculated and given in Table 6 (numbers rounded off).

Table 6. Re-vamped Table 4 - Regulations in 8 hour TWA format

<u>Threshold Limit Values (TLV)</u>	
W Germany	12 ppm (8 hr TWA) - existing factories 5 ppm (") - new factories
Belgium	6 ppm (")
Denmark	1 ppm (") - <u>PVC fabricators</u> - <u>personal</u>
Finland	5 ppm (") - <u>personal</u>
UK	10 ppm (")
Sweden	1 ppm (") - <u>personal</u>
Switzerland	12 ppm (") - <u>personal</u>
USA	1 ppm (") - <u>personal</u>
Proposed EEC	7 ppm (")

As you are well aware, to meet such limits consistently with 95% certainty, one has to be working on average at half the above limits eg to meet 10 ppm one must work at 5 ppm or below. A graph of a typical UK plant is given in Table 7.

TABLE 7. WEEKLY AVERAGE VCM LEVELS IN ATMOSPHERE
(SUSPENSION POLYMER PLANT)



In the USA if readings taken in a specified schedule are all below 0.5 ppm, the plant is exempted from the provisions of the relevant OSHA regulation for VCM - this is the mechanism whereby PVC fabrication plants in the USA are regulated.

I have underlined the word personal in the above tables. While one can measure the VCM in a gas sample taken from a working area with a sensitivity of 0.1 ppm GLC, 1 ppm FID, 0.5 ppm IR and 0.2 ppm Photo Ionisation, the actual exposure of employees in the particular working area or in the plant cannot be measured with the same degree of accuracy. For example a strategy may be adopted to have sampling points at those places where there is the greatest chance of leaks. At those points there may be no one exposed or, if he is exposed, he may be exposed only intermittently and if there is a leak, he may be in breathing apparatus and not taking in VCM. The techniques for coping with these problems vary from country to country (and indeed company to company). In some countries, the average is taken of all the readings over an 8 hour shift for a working area and whether the employees are exposed or not, the average is called the 8 hour TWA. In other countries, an activity analysis is worked out for each employee and his personal exposure is worked out from the average area exposure in each working area and the time he spends in that area. In some countries where the ceiling exposure above which gas masks must be worn is eg 15 ppm, the 8 hour TWA is worked out on the above bases but omitting any area readings above 15 ppm. One must not therefore look at Tables 4 and 6 and make invidious comparisons or judgments about the stringency of hygiene in the various countries.

To my mind by far the best and fairest solution has been adopted in the UK where the Code of Practice, worked out by a tripartite group of representatives of government, unions and employers, gives detailed guidance on monitoring strategy. The strategy and the results of the monitoring are open to inspection and discussion at all times. In practice, there have been few problems. So far as we can discover, nearly all VCM and PVC factories in the Western world of similar age and design, with similar product ranges have roughly the same hygiene standards despite the spread in figures in the regulations. We await with interest to see how the EEC attempt at harmonisation works out - the 1 year average has been christened the Technical Long Term Limit Value (TLTLV) and is in the nature of an experiment. I hope the EEC will give us a few years to get results from this experiment before they attempt to extend the use

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of this concept which is ill understood and to some extent mistrusted by many people in Europe.

The problems of defining alarm levels, action levels, intervention levels, MAK values, TRK values, STEL values (short term exposure levels) etc. are perhaps more appropriate for another occasion. I should like to close this talk by referring to the problems of monitoring VCM in the PVC fabrication industry. In Europe there was great disappointment in some quarters that the above draft EEC Directive excluded fabrication. The Commission has been asked by its statutory advisory bodies to propose a special draft directive to cover the PVC fabrication industry. Some countries think this is a complete waste of time and money since spot checks show that working area atmospheres are generally less than 1 ppm and it would be very costly to set up sequential monitoring equipment and institute medical surveillance and 30+ year record keeping facilities for all employees. PVC manufacturers are continuing to reduce the VCM content of PVC polymer and at least one government (West Germany) has drafted a regulation which stipulates that PVC polymer must contain < 10 ppm VCM to safeguard employees in PVC fabrication plants. My own personal view is that there is no need for legislation - no health problem associated with VCM has been found to date in the fabrication industry. So far as we can determine, the health problems have been confined to the former autoclave cleaners who form part of the 30,000-50,000 population in the World PVC manufacturing industry. With a much greater population of at least 1 million people involved in PVC fabrication in the World, only 3 ASL cases dubiously related to VCM have been listed. One would have expected to have uncovered any health difficulties by this time, especially since many researchers have been and still are actively investigating this area.

Over the past 4 years the PVC industry has learned to monitor and control VCM in VCM and PVC manufacturing plants, in PVC products, in the PVC fabrication industry and in the environment by the extension and application of GLC, IR, FID, etc. technology. Perhaps in the next few years we shall see these monitoring methods complemented by the use of remote sensing devices based on infra red laser technology and particularly the use of short intense light pulses in LIDAR (Light Detection and Ranging) techniques. We look forward to the development of such open path, remote sensing environmental analysis techniques in the hope that they will help us to improve safety, health and hygiene in our industry.

J Stafford
Division Manager
Health & Environment Protection

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