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Chapter 3

TOXICITY AND VINYL CHLORIDE

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SUMMARY

After nearly 50 years of commercial production of PVC, vinyl chloride monomer was found to be a human carcinogen. The following chapter describes how contact with vinyl chloride both in the work place and in consumer applications has been reduced to a level where no major hazard exists to health. Data are presented showing how great the progress has been with the problem since it was first recognised at the end of 1973. The technology used to bring about such results is reviewed. Further progress will be significantly less dramatic. Although the health precautions taken have led to an increase in the manufacturing costs of PVC, it remains an essential component of present-day civilisation. There is, in fact, an increased awareness of its remarkable versatility.

3.1 INTRODUCTION

Some future historian of the chemical industry will, in retrospect, point to the vinyl chloride (VCM) problem as a landmark in the progress of its offshoot, the plastics industry. Long periods of exposure to a substance hitherto regarded as relatively medically safe led to the appearance of a number of occupationally related diseases, including a rare form of incurable liver cancer—angiosarcoma of the liver.

The intensive investigations set in train by this discovery are by no means complete—nor is the development of improved manufacturing methods and procedures to reduce still further the traces of VCM escaping into the

atmosphere (in polymerisation and fabrication plants) or, migrating into foodstuffs (albeit in minute quantities). Medical research programmes continue into improved and early diagnosis of VCM-related diseases as well as into understanding the mechanisms of its various effects.

In spite of the fact that any report on the problem must, to some extent, be regarded as interim, the PVC industry can point to considerable progress made during the last three years in solving the various technical problems encountered in reducing any possible hazard to a socially acceptable level.

The author has been actively involved in one of the UK Working Parties dealing with the VCM problem and has first-hand experience of the extensive co-operation among companies (both national and international), trade unions and government agencies in order to bring about a speedy solution to the various problems. In spite of the differences of detail, broadly similar approaches to problem resolution have been employed around the world. There are useful accounts of the problem seen through German eyes,[37] and through American eyes;[11] the latter includes a chronology of key events.

3.1.1 Background to the Problem

Large scale production of PVC resins by the polymerisation of VCM started in the 1930s. Although the hazards of fire, explosion and narcosis were well recognised, there was no evidence to suggest that VCM constituted a health hazard; indeed it had been suggested that it would have been adopted as an anaesthetic, but for the fire and explosion hazard.

The first work suggesting a potential for carcinogenicity came from studies carried out by Viola and co-workers in an attempt to reproduce acro-osteolysis in rats.[1] (Suggestions that Russian workers had observed liver damage amongst polymerisation workers as early as 1949 are unfounded.[3] The study related, in fact, to 48 workers compounding PVC with chlorinated diphenyl). Acro-osteolysis, Raynaud's Syndrome and scleroderma had been observed amongst some PVC polymerisation workers, particularly those involved in the manual cleaning of deposits from autoclave interior walls. The act of removing deposits of encrusted PVC resin releases unreacted VCM and it is this VCM which presumably causes diseases such as acro-osteolysis—a vascular disturbance.

The clinical findings may be, for example:

1. Increased sensitivity to cold,
2. Pins and needles and other paraesthesia, and
3. Changes in the colour of the skin of the digits.

These are the signs of a disturbance known as Raynaud's Syndrome. Another feature of the acro-osteolysis may be changes in the bone pattern of the terminal phalanges, often accompanied by deformation of the nails.

Scleroderma is the medical term for the thickening of the skin which can occur as a result of contact with VCM, and it can lead to gross deformation of, for example, the thumbs.

In studies reported in 1971, Viola showed that exposure of rats to atmospheric concentration as high as 30 000 ppm (parts per million) failed to produce acro-osteolysis. However, malignant tumours were found.

The level of exposure of the rats was so high that its significance to human beings was not clear and further work was necessary. A consortium of European interests, including ICI Limited (UK), Rhone-Poulenc-Polymeres (France), Montedison (Italy) and Solvay (Belgium) commissioned Professor Cesare Maltoni to carry out further studies. Cancers were confirmed in animals at exposures as low as 250 ppm, including angiosarcoma of the liver.[2]

Maltoni's findings led to an epidemiological survey being conducted in the USA on men who had previously worked in a PVC polymerisation plant (B. F. Goodrich, Louisville, Kentucky). This study revealed a cluster of cases of the exceedingly rare form of cancer, angiosarcoma of the liver. The results of this study group (by Creech and Johnson) were transmitted to the National Institute of Occupational Safety & Health (USA) on 22 January 1974, the Department of the Employment (UK) on 23 January 1974 and the Acting Chief Employment Medical Adviser (UK) on the next day. Other national governments were notified during the same period.

In the UK on 29 January 1974, ICI issued a press statement announcing that government departments, the TUC, its own workers and customers, were being informed of the facts available so far concerning the urgent investigations into the cause of death of a seventy-year old retired autoclave worker. It was subsequently confirmed that the worker, who had died in 1972, was suffering from angiosarcoma of the liver. During his working life he had undergone twenty years exposure to VCM.

In February 1974 the Chemical Industries Association in the UK formed a Vinyl Chloride Committee to study the whole problem and institute necessary programmes of work through a series of specialised working parties. Similar arrangements were made in other countries of the world. In Europe international co-operation was ensured through CEFIC (Conseil Europeen de Federations de l'Industrie Chimique) which formed its own Vinyl Chloride Committee with national representatives taking decisions on behalf of their colleagues.

3.1.2 Extent of the Vinyl Chloride Problem

At the end of 1976 the number of notified angiosarcoma deaths was fifty-five. The distribution of deaths is shown in Table I.

The average length of exposure before death was 15–20 years. Almost without exception the deceased had worked on polymerisation plants and had been engaged in the manual cleaning of autoclaves during part of their service. Certain plants show a clustering of deaths.[6]

TABLE I

NUMBER OF NOTIFIED DEATHS FROM ANGIOSARCOMA (UP TO THE END OF 1976)

Country	*Number of deaths*
Belgium	1
Norway	1
UK	2
Italy	3
Sweden	3
Eastern Europe	4
France	6
Germany	7
Canada	10
USA	18

Crampton[6] and other authors[4] describe other disorders caused by VCM. These include acro-osteolysis (approximately sixty-five cases in the world—all autoclave cleaners), associated Raynaud's Syndrome and scleroderma, and liver dysfunctions. This latter group of disorders has sometimes been referred to as 'PVC Disease'.[7]

Most of the workers suffering from this group of disorders were polymerisation workers and particularly those manually cleaning autoclaves.

Whilst some disagreement exists on the severity of the effects of the other groups of disorders, angiosarcoma of the liver is invariably fatal.

Studies on the carcinogenicity of VCM, whether by inhalation or ingestion, will not be complete for some considerable time. Until a medically proved acceptable exposure level is established, the object of much of the work has, during the last three years, been to reduce possible exposure to VCM to as near zero as possible.

In the meantime, epidemiological surveys of polymerisation workers have been carried out in the UK, the USA and elsewhere to establish the possible extent of the problem.

Other work has been directed at improved diagnostic methods to give advanced warning of problems.[4,8]

Yet further work has been aimed at understanding the mechanism of the way in which VCM causes angiosarcoma of the liver. Tentative hypotheses have been advanced involving the role of metabolites of VCM, such as chloroethylene oxide and modification of DNA molecules.[5]

Although no final conclusions can yet be drawn from the medical work carried out, some authorities have attempted an assessment of the risk from VCM in the light of recent performance. The results are encouraging.[9,10]

Whilst there must inevitably be an element of speculation in assessing all medical work, the results of work by the PVC industry are demonstrable. These will be described in the following pages.

3.1.3 Sources of Interface Between Human Beings and VCM

To understand the problem and the progress made in containing it, a brief account of the processes for the manufacture of PVC resins, compounds and finished articles is necessary.

VCM is a gas boiling at −13·5°C. It is therefore necessary to polymerise it under pressure. Commercial resins are made generally by polymerising 70–90% of the VCM. This leaves a quantity of unreacted gas within the autoclaves as well as within the particles of the PVC resins. Complete reaction of the monomer is not feasible. If made by the suspension or emulsion processes (accounting between them for the majority of world PVC production) it is necessary to separate the water present, for example by centrifuging and drying. All these processes lead to the release of further quantities of VCM. Finally, the resin itself will still contain small quantities of unreacted monomer, particularly those resin types with dense glassy particles used for direct powder blend processing, e.g. in the extrusion of water pipe or extrusion blow moulding of bottles.

Subsequent processing operations involving the use of heat will lead to further releases of VCM. Small quantities remaining in the finished articles will be released by slow diffusion. In the case of packaging materials, very small quantities of VCM may be transferred into foodstuffs and beverages. There is also the possibility of transfer of very small traces of VCM into drinking water supplied through PVC pipes.

3.2 DEVELOPMENTS IN REDUCING CONTACT WITH VINYL CHLORIDE

The preceding section identified the possibilities of exposure to VCM in the following areas:

1. Polymerisation and associated operations,
2. Storage and handling of PVC resins,
3. Hot processing of PVC compounds,
4. Fabrication of finished products, and
5. Diffusion from finished products, including migration into foodstuffs and drinking water.

Before considering the developments that have taken and still are taking place, some estimate of exposure levels is appropriate. Before the realisation that excessive exposure to VCM could lead to crippling or even fatal illnesses, little reliable data on atmospheric VCM levels around polymerisation plants was available. Table 2 gives such information, and is based on more recent measurements and earlier estimates.

TABLE 2
VCM LEVELS AROUND POLYMERISATION PLANTS

Year	*Typical average level (ppm)*
1945–1955	500–1 000
1955–1960	400–500
1960–1970	300–400
Mid-1973	150
Mid-1975	5
End 1976	2–5

Levels encountered in the fabrication and end use sectors are given in Table 3.

TABLE 3
TYPICAL RECENT VCM LEVELS (PPM)

Location	*January* 1974	*July* 1975	*December* 1976
In plant atmospheres	2·15	<2	<1
In PVC bottles	~50	~2	<1
In beverages	0·1	0·01	<0·005

Estimates of the intake of VCM have also been made;[4, 5] these are shown in Table 4.

As expected, the figures show that the intake of VCM by polymerisation plant workers was by far the most significant. As will be shown, many of the steps taken to reduce the exposure of polymerisation workers to VCM led to improvements in downstream activities.

TABLE 4
ESTIMATES OF DAILY VCM INTAKE

Type of person	*Daily VCM intake (g/kg body weight)*
Polymerisation worker at	
1 000 ppm	0·36
500 ppm	0·18
5 ppm	0·001 8
2 ppm	0·000 7
Fabrication plant operator	
1 ppm	0·000 4
European citizen—through ingestion of food	0·000 000 002–0·000 000 008

3.2.1 Polymerisation Plant Developments

The level of VCM permitted in the atmosphere about polymerisation plants, the absolute quantities which may be emitted into the atmosphere, the quantities which may be present in waste water and in some cases the quantities remaining in PVC resins, are the subject of various compulsory national regulations or voluntary codes of practice and hygiene standards. They vary in detail and in the methods of calculating certain required numerical data, in particular average and peak personnel exposure results. These apparent differences obscure the general similar level of achievement in most countries of the world.

Typical average levels of atmospheric VCM about PVC polymerisation plants are now 2–5 ppm; this has been achieved by improving the operating procedures in a number of ways:

1. More efficient degassing of the PVC resin, either in the polymerisation autoclave or downstream from the autoclave, resulting in lower losses at the drier stage. Much effort has been

expended on the development of improved degassing systems and a number of patents have appeared.[19,23,31,32,33] The B.F. Goodrich process for counter-current stripping of resin slurry has been licenced to a number of other PVC resin producers.

2. Development of automated high pressure washing methods for autoclaves so as to avoid the necessity of entry and manual cleaning.
3. Development of autoclave surface-treatment systems which reduce the tendency of crusts or skins to form, so reducing the amount of cleaning necessary.[12,13,18,20,21,24] The Shin-Etsu Company of Japan and the B.F. Goodrich Company of the USA have licenced their technology to a number of other PVC resin producers. Other companies have reported the use of additives in polymerisation recipes which reduce encrustation.[14,22,34]
4. Remote operation of autoclaves which may often be controlled by a computer. This technique will grow in importance as a result of recent spectacular explosions, such as that at Flixborough.
5. The use of larger autoclaves, so reducing the number of flanges and valves, etc. for a plant of given output. Such developments were under way before the health problem of VCM was appreciated. The largest reported commercial autoclaves are those operated by Chemische Werke Hüls—200 m^3. B.F. Goodrich operates a plant at Louisville with autoclaves of 62 m^3. The Shin-Etsu Company of Japan uses autoclaves intermediate in size at 130 m^3. All three companies have licenced their larger autoclave technology.
6. Development of recipes and agitation systems yielding more uniform resin particles. Uniformity of resin particle structure is a requirement of the industry, irrespective of the VCM problem. Added impetus has been given to the work since a more uniform particle structure will lead to more uniform degassing. Especial priority has been given to investigations into the production of resins for such applications as water pipe and bottles which normally start from a powder blend. Processing rates are influenced by bulk density and particle shape. The problem is to produce resins with a regular shape and porous structure and at the same time an acceptable bulk density. Some progress has been made towards this objective.
7. Use of respirators by personnel when carrying out operations in areas with unacceptably high atmospheric levels of VCM.
8. Development of automatic sensitive monitoring systems scanning all working areas.

Outstanding problems still exist, notably in reducing losses from certain downstream stages after the autoclaves. The Environmental Protection Agency in the USA has set very stringent requirements which may prove difficult to achieve.[28]

Abramowitz[30] gives a useful account of progress in mass polymer plants.

Some quality problems have inevitably arisen as a result of producers finding themselves forced to bring about rapid improvements with existing equipment or incompletely developed modifications. These considerations, as well as long delivery times of some equipment, have forced companies to use ad hoc interim arrangements. For example, reductions in residual VCM have been effected by the expedient of more severe drying conditions leading to poorer resin colour and stability, poorer flow in hoppers (due to static electricity effects) and reports of different fusion characteristics (probably attributable to subtle surface changes due to the higher drier temperatures).

The cost of modifying some plants has resulted in their closure. Reduction of approximately 10% of plant productivity has occurred in many cases, and production costs have increased by an average of 10–15%. On the other hand, VCM utilisation efficiencies are markedly improved. A further benefit is that the reduced necessity to enter autoclaves for cleaning has improved working conditions.

3.2.2 Reductions of VCM Exposure in Handling, Processing and Fabrication

The preceding section refers to steps taken to reduce residual VCM levels in PVC resins. Some resin particles are more difficult to degas effectively than others. For rigid extrusion, extrusion blow moulding and injection moulding operations (using a powder blend feed rather than a fully compounded granule), dense regular particles are required in order to obtain good powder flow and efficient packing of screws. Such PVC resins retain VCM more tenaciously than those with an open particle structure used for the manufacture of plasticised compounds and plasticised finished products. In early 1974 it was common for such resins to contain 1000–2000 ppm residual VCM. In some cases even more was retained, e.g. in homopolymers made by the mass polymerisation route, and acetate copolymers.

VCM is slowly released from the polymer at room temperature. At elevated temperatures such as those encountered during processing the release is extremely rapid. In the USA, there are reports of VCM accumulating in the free head space of rail cars until the levels reached are

potentially capable of explosion. In Europe, fires have occurred at the vents of extruders processing rigid powder blends.[16]

In the early part of 1974, extensive surveys of more than 100 companies were carried out in the UK, in order to establish the levels of VCM encountered during processing and handling operations. The findings[17] are shown in Table 5.

TABLE 5
ATMOSPHERIC VCM LEVELS AROUND PVC PROCESSING AND FABRICATION OPERATION (PPM V/V)

Location	*Range*	*Average*
Polymer warehouses	<2–17	2
Cold mixing equipment	<2–3	<2
High speed mixing[a]	<2–53	3
Banbury type mixer	<2–13	2
Two-roll mill compounding	<2–2	<2
Paste mixing	<2–16	<2
Calendering	<2–3	<2
Fabric and paper coating	<2–5	<2
Pipe extrusion	<2–7	<2
Cable extrusion	<2–4	<2
Injection moulding	<2–4	<2
PVC welding	<2	<2
Vacuum forming	<2	<2
Bottle blowing	<1–2	<1
Extrusion of flexible film	<1–2	<1
Extrusion of rigid sheet	<1–4	<2

[a] Single result of 53 with high acetate copolymer at bin filling point.

Most of the results were of a low order, averaging 2–3 ppm. However, certain unacceptable practices came to light. High speed mixing areas were particularly prone to unacceptably high atmospheric levels. This was not surprising since at temperatures in excess of 110°C, PVC resins release VCM very rapidly.

Improved operating procedures, such as the installation of localised extraction, the venting of extruders and mixers to the outside of buildings, and good general ventilation in warehouses etc., resulted in levels below 2 ppm by early 1975. By the latter part of 1976 the effects of reducing

residual VCM in PVC resins have resulted in levels generally below 1 ppm with many results at 0·1–0·2 ppm; near the limit of detection of the analytical methods used.

3.2.3 Potable Water Supply

Virtually all potable water pipe is produced by extrusion from powder blend. Although some differences in formulation practice have developed with, for instance, Europe favouring the use of solid lead salts as stabilisers and the USA favouring the use of liquid tin compounds, a common feature of the pipe-making industry was the increasing use of high bulk density resins to increase extruder outputs.

As reported earlier, such resins tend to retain residual VCM more tenaciously, and levels of 1000 ppm or more were not uncommon.

As well as the necessity to reduce residual VCM levels in new pipe production, measurements on drinking water passing through existing pipe systems were required.

At one location in the UK, the Chemical Industries Association was able to carry out measurements on drinking water supplied entirely through a rigid PVC pipe network manufactured by one company. The pipes were 102 mm (4 in) and 152 mm (6 in) in diameter. Even in those parts of the network where PVC resins containing 1000 ppm residual VCM had been employed to manufacture the pipe, no VCM could be detected in the drinking water.

Further studies were carried out on houses connected by small bore PVC and chlorinated PVC pipe. Here, a more unfavourable surface/volume ratio could be expected to increase the possibility of extraction of VCM; however, only at one location could any VCM be detected. This was in a home built some nine or ten months previously and unoccupied since completion. In the small volume of water which had stood in contact with the PVC pipe, 0·015 ppm of VCM was detected.[25]

The above results were extremely encouraging. Nevertheless, three lines of attack were used to reduce VCM levels in rigid PVC pipe:

1. Increased use of hot (i.e. >110°C), high speed mixing, combined with aeration, in the preparation of the powder blends. Some companies had originally only mixed to relatively low temperatures, i.e. 70–80°C.
2. Improved degassing techniques during PVC resin production. Typical average residual VCM levels for pipe resins are now in the 5–50 ppm range.

3. Development of suspension resins of increased porosity. A judicious selection of suspending agent combinations, or other appropriate formula modifications in the case of mass polymer, can produce resins with regular particle shape, significantly increased porosity and only a marginal sacrifice in bulk density. Further developments can be expected by this approach.

A combination of the above approaches has led to significant reductions in the residual VCM levels in rigid PVC potable water pipe and some companies are now achieving average levels of less than 1 ppm.

Both the Ethyl Corporation in the USA and ICI in the UK have determined the diffusion coefficient of VCM from rigid PVC pipe. The results have been used to predict VCM levels in drinking water supplied to typical households, in the USA and the UK, using pipe with 1 ppm residual VCM.[26] For the UK, the level of VCM in the water is predicted to lie between 0·006 ppb and 0·022 ppb (b = 1000 million). In the USA the predicted values are 0·01–0·14 ppb. Not surprisingly, the use of liquid tin stabilisers in the USA in place of solid lead salts in the UK gives a higher coefficient of diffusion.

Since most water consumed is used in cooking or in the preparation of hot beverages, with attendant further loss of VCM, the average levels in consumed water are decreased even further.

3.2.4 Food Packaging

Any review of the use of PVC for food packaging must, in the light of the VCM problem, take into account both the political background of legislation and the variations in usage in different countries.

In the USA, the Food and Drugs Administration (FDA) is constrained by precedents set in the interpretation of the so-called Delaney Clause of the Food, Drug and Cosmetic Act of 1958 which states 'No additive shall be deemed to be safe if it is found, after tests which are appropriate for the evaluation of the safety of food additives, to induce cancer in man or animal. . . .'

At the time of its introduction, the above clause was clearly intended to be interpreted in the light of testing, probable consumption levels, safety margins and reasonable certainty about conditions of use. In practice, precedent has established the clause as intending to mean a total ban on any additive suspected of causing cancer under any conditions.

As a result of this, American legislators are not free to make a truly scientific assessment of a possible carcinogenic hazard. Any regulation which falls short of a total prohibition is, in fact, a politically influenced decision.

In this situation the FDA produced a new form of words in a proposed regulation issued in September 1975. The proposals permitted the continuing use of PVC in contact with foodstuffs 'where the potential for migration of vinyl chloride is diminished to the extent that it may not reasonably be expected to become a component of food.' Against this definition the FDA proposed to allow the continuing use of flexible film and hose. Rigid and semi-rigid foils and bottles would have their status of prior sanction withdrawn. Any producer of the latter group of products would then be obliged to demonstrate that they met the FDA criterion.

At the time of writing no decision has been taken on the proposals and it is extremely difficult to predict the outcome.

In the United States the most important outlet for PVC in food packaging is in plasticised films such as meat wrap. On the other hand, the use of rigid PVC is relatively less important and in particular the use of rigid PVC bottles for food packaging has scarcely developed. Therefore, whatever the decision its economic effect on the United States packaging industry will be relatively small.

The EEC is slowly moving towards a unified approach on food packaging legislation, and no matter how much European countries may wish to display their independence of events in the USA, in practice, packaging legislation in the latter country has previously influenced events in Europe. In the case of PVC and VCM, however, the EEC produced a draft directive at the end of 1976 which takes into account the realities of the situation in Europe.[27] Since a 'no effect' level has yet to be established for VCM, the proposed directive takes into account the best practical achievements of European industry in reducing VCM levels in PVC food packaging. Before discussing these achievements, some account of the variations in European food packaging practices is necessary to understand the basis of the proposals. Whilst plasticised PVC films are important for food packaging in Europe, the use of rigid PVC bottles or foils is especially important. Certain countries in Europe show marked variations in the pattern of usage. In France for instance the manufacture of rigid PVC bottles for mineral water is a major industry, accounting for 100 000 tonnes of PVC compound in 1976, whereas in Germany, rigid PVC foils account for the major proportion of rigid PVC used in food packaging.

In the UK a major proportion of rigid PVC bottles is used for the packaging of fruit squashes. Such squashes are mainly consumed by young children, a section of the population for whom there is special concern.

There are also some significant differences in formulating practice in Europe. In France and countries subjected to French influence, most bottles are based on tin-free formulations. Such formulations contain significantly higher levels of other liquid additives to help processing. In Germany particularly, tin stabilisers are preferred.

Whilst there is a significant usage of tin-free bottle formulations in the UK, the majority are based on tin stabilisers. Most rigid PVC foils in Europe are based on homopolymers, but in the UK a significant percentage of production (circa 75%) is based on acetate copolymers.

TABLE 6
VCM LEVELS IN UK-MANUFACTURED PVC PACKAGING MATERIALS

VCM location	*VCM concentration (ppm)*		
	January 1974	*March* 1975	*December* 1976
Bottles			
Level in polymer at time of use	500–1 000	100–250	15–50
Typical level in powder blend at time of manufacture	50	5	1
Typical level in bottle wall	50	3	< 1
Foil			
Level in polymer at time of use	800–1 500	100–250	50–100
Typical level in foil	80	8	3
Flexible film (extrusion blown)			
Level in polymer at time of use	400–1 000	50–150	5–30
Typical level in film	1	1	< 1

Table 6 shows the residual VCM levels in UK-manufactured PVC packaging materials during the three-year period January 1974 to December 1976. It will be noted that in the case of flexible film, residual VCM levels were very low, even at the beginning of the period under review. This is explained by the fact that the presence of plasticiser aids the release of VCM during hot processing.

The higher levels of residual VCM in rigid foil compared with bottles is explained by the use of copolymers in the manufacture of the former material. The relatively low softening point of copolymers makes it extremely difficult to achieve low VCM levels either at the resin-making stage or during mixing. For the foreseeable future copolymer foils are likely to contain slightly higher residual VCM levels than bottles or foils based on homopolymers. Since most such foils are either used for the packaging of solid foodstuffs or materials of restricted shelf life, the slightly higher level in the package does not normally lead to higher levels in foodstuffs.

The results shown in Table 6 are also generally typical of the position in Europe as a whole with two provisos:

1. Where homopolymers are used to manufacture rigid foils, residual VCM levels are lower and more in line with UK results for bottles; and
2. Where tin-free stabiliser systems are used in bottle formulations, the presence of extra liquids and low melting point additives assist the displacement of VCM during processing, and residual levels in such bottles will tend to be lower than in bottles based on tin stabilisers.

Some important conclusions can be drawn from Table 6:

1. Flexible film has low residual VCM levels even at the beginning of 1974. Subsequent improvement has only been marginal;
2. Rigid PVC has shown a marked improvement, especially during the period January 1974–March 1975;
3. Since current USA achievement does not differ significantly from that in Europe, the logical course for the Food and Drug Administration would be to accord rigid and semi-rigid PVC the same status as flexible film, i.e. continuing prior sanction.

3.2.5 VCM in Packaged Food

Numerous studies have been carried out on the migration of VCM from the package into the contents. In the UK regular surveys have been carried out on random samples from retail outlets. The results of this large body of continuing work may be summarised as follows:

1. Under ambient conditions rigid PVC packages lose part of their residual VCM to the atmosphere; after a year approximately 30% has been lost in this way;
2. VCM reaches an equilibrium concentration in the contents of packages after several months;
3. This equilibrium concentration allows typical partition concentrations to be calculated. For foodstuffs commonly packaged in PVC in the UK the concentration of vinyl chloride remaining in the PVC is 200–700 times that present in the contents;

4. Only very small proportions of the VCM in a package may transfer to the contents and for a wide range of foodstuffs the levels of extraction are similar; and
5. Under certain circumstances small numbers of packages may remain on retail shelves for far longer than the recommended shelf life of the contents.

The use of the partition data enables calculations to be made of expected maximum VCM contents of foodstuffs packaged in rigid PVC.

Extensive retail surveys have provided firm support for such predictions. At the end of 1976, VCM levels in foodstuffs packaged in the UK were in the range 0·003-0·005 ppm or less.

Work carried out both in the UK and in Continental Europe has shown that the equilibrium partition concentrations with tin-free bottle formulations such as those typically used in France are not as favourable as those with tin stabilised formulations. For some foodstuffs the ratio of concentration of vinyl chloride in the bottle to that present in the contents may be as low as 100. This disadvantage is, to some extent, offset by the fact that VCM tends to be displaced more readily during hot processing, giving slightly lower initial levels in the bottles.[28]

Gilbert[29] also has suggested that at low initial concentrations in bottles and other rigid containers, extraction of VCM by foodstuffs will be less than expected because of the presence of active sites in the matrix of the PVC which retain VCM.

A further factor influencing the EEC proposals is the state of development of suitable analytical techniques. With some foodstuffs problems of interference exist. Also, even in the hands of highly skilled research analysts, it is very difficult to get agreement between different laboratories.

Finally, the manufacturer of the PVC container or foodstuff must be able to observe trends in the VCM content of his products and take corrective action. For this to be possible, the maximum allowable VCM must be rather more than that at the limit of analytical detection.

Against this background the EEC has produced its draft directive. The main features of the directive are:

1. A limit of 0·050 mg/kg in the foodstuff (i.e. 50 ppb);
2. A limit of 1 mg/kg in the container (i.e. 1 ppm); and
3. In the case of containers made from copolymers, a limit of 5 mg kg, provided that they are not used for liquid foodstuffs.

It is too early to predict the success of the proposals. However, similar requirements or recommendations already exist in some European countries.

For further information on VCM and PVC packaging the reader is referred to the publications of GECOM (Groupe d'Etude Pour le Conditionnement Moderne). GECOM was founded in France and is an association of PVC producers and the manufacturers of packaging and foodstuffs, including water, oil and wine. It was set up to study the various problems in the packaging field raised by the discovery of the toxicity of VCM. The address of GECOM is 11 Rue Marguerite, Paris 17. One of the GECOM publications gives a very useful account of the problems of analysis of foodstuffs containing vinyl chloride.[38]

3.3 ANALYSIS AND DETECTION OF VCM

The progress described in the preceding pages would not have been possible without significant advances in the methods of detecting VCM. Developments have taken place in three major areas:

1. The monitoring of atmospheric levels of VCM in the vicinity of polymerisation plants;
2. Analysis of VCM, often present only in minute traces, in PVC resins and compounds, food packaging and foodstuffs; and
3. Small portable detectors.

3.3.1 Monitoring of Atmospheric Levels

Prior to 1974 the measurement of VCM was a time-consuming process and the methods required development so that they were capable of yielding accurate results at great speed and were suitable for the sequential scanning of working areas on polymerisation plants.

Two methods of analysis have gained particular favour for the task:

1. Gas chromatography combined with a flame ionisation detector; and
2. Infrared absorption.

In the first method samples of air are drawn through a suitable column which separates VCM from other possible airborne contaminants. The VCM fraction is burnt in the presence of pure hydrogen, forming ions which are then measured by an electrical technique.

This method is very sensitive and can measure fractions of 1 ppm of VCM.

The second method depends upon the fact that VCM absorbs infrared radiation at a number of wavelengths which are characteristic both of the

unsaturation and of the carbon–chloride bond. The amount of radiation absorbed depends on the amount of VCM in the beam of radiation. In the equipment used in PVC plants, the optical system is designed so that the beam of radiation is repeatedly reflected between a pair of mirrors to give an absorption path length of more than 20 metres. This means that the equipment is of reasonable size, yet it can still detect concentrations of less than 1 ppm.

Both methods are in widespread use in PVC polymerisation plants, drawing in samples of air from a large number of points which are scanned sequentially every few minutes.

Such instruments are often used in conjunction with specially designed computers which permit rapid calculation of shift averages and analysis of excursions above hygiene standards. As an example of what is being achieved by such techniques, see paragraph 37 of the 'Vinyl Chloride Code of Practice for Health Precautions' issued by the Health and Safety Executive in February 1975.

3.3.2 Detection in Foodstuffs

VCM may occur in both PVC resins and articles fabricated from PVC where the concentration may range from fractions of 1 ppm to hundreds of ppm. However, in the case of foodstuffs the range is parts per billion. Quick, reliable methods of analysis were required to allow control of PVC manufacturing processes as well as to assess the progress in reducing the minute traces migrating into foodstuffs. The method which has gained general acceptance for such work is the so-called headspace method.[36] In this method, the sample is dissolved in a suitable solvent and allowed to equilibrate in a small vial. Gas from the headspace, consisting of a mixture of the solvent and VCM, is passed through a gas liquid chromatographic column and the peak due to VCM is measured. Systems are available which permit the automatic measurement of pre-loaded samples in a typical measurement time of thirty minutes. A number of solvents are used, such as tetrahydrofuran and dimethylacetamide.

In the case of PVC resins and objects, the method is capable of measuring fractions of 1 ppm of VCM. With some foodstuffs the method will detect a few parts per billion, whereas with others there are serious interference problems.

3.3.3 Portable Detectors

A number of miniature detectors have been developed which may be worn by plant personnel so that personal exposure levels can be measured directly. All types depend on the oxidation of VCM to hydrochloric acid or chlorine. These substances then stain specially treated paper, and the intensity of the stain gives an indication of the intensity of the concentration of VCM.

Such instruments will measure from fractions of 1 ppm up to 40 ppm, depending on the equipment.

A Chemical Industries Association publication[36] gives details of reliable analytical and detection methods.

3.4 CONCLUSIONS

Due to the long latency period of angiosarcoma of the liver, it is inevitable that some further cases will occur. However, there is no doubt that the major hazards associated with VCM have been corrected. Some further improvement in reducing atmospheric levels and the levels of VCM remaining in PVC resins will occur, but the improvements will be relatively marginal compared with what has already been achieved in so short a time.

PVC continues to remain an essential component of present day technology with an improved awareness of its remarkable versatility and usefulness.

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REFERENCES

1. VIOLA, P. L., BIGOTTI, A. and CAPUTA, A. *Cancer Research*, 37 (1971), 516.
2. MALTONI, C., CRESPI, M. & BURCH, P. J. R. *Excerpta Medica International Congress*, Series No. 275, 1973.
3. BARNES, A. W. National and international aspects of the VCM health problem. Part II. Paper given at the *BPF/PRI Joint Conference: Vinyl Chloride and Safety at Work*, 28 May 1975.
4. *Proceedings of the Royal Society of Medicine Section of Occupational Medicine*, 69, April 1976.
5. *Vinyl chloride toxicity and the use of PVC for packaging foodstuffs.* A presentation by the CEFIC Committee for the Toxicity of Vinyl Chloride. February 1976.
6. CRAMPTON, R. F. Assessment of toxic risks to workers in the plastics industry. *BPF/PRI Joint Conference Vinyl Chloride and Safety at Work*, 28 May 1975.

7. *VC/PVC: An Example of a Problem Resolved*, Verband Kunststofferzeugende Industrie e V Frankfurt am Main, West Germany, 15 September 1975.
8. WILLIAMS, D. M. J., *et al. Brit. J. Indus. Med.* 33, (Aug. 1976) pp. 152–7.
9. WILSON, R. *Risk benefit analysis for toxic chemicals: vinyl chloride*. Paper given at the 172*nd ACS National Meeting*, San Francisco, 25 August 1976.
10. SCHLATTER, Ch. 'Gefährdung von Arbeitnehmer und Konsument durch Vinyl Chlorid.' Press Release by Lonza AG, 29 October 1975.
11. 'PVC and Health.' A background statement issued by the Society of Plastics Industry Inc., New York, April 1976.
12. British Patent 1 291 145.
13. British Patent 1 421 718.
14. British Patent 1 444 360.
15. Federal Register, 21 October 1976, 41, No. 205. Environmental Protection Agency, National Emission Standards for Hazardous Air Pollutants, Standard for Vinyl Chloride.
16. Private communication.
17. CLAYTON, H. M. Guide lines for PVC processors. Paper given at the *BPF/PRI Joint Conference Vinyl Chloride and Safety at Work*, 28 May 1975.
18. Belgian Patent 833 558.
19. Belgian Patent 831 964.
20. Belgian Patent 833 041.
21. British Patent 1 407 665.
22. Belgian Patent 837 070.
23. British Patent 1 446 583.
24. US Patent 3 669 946.
25. MOFFITT, T. W. Private communication.
26. MOFFITT, T. W. Private communication.
27. Document 1565/VI/76-F.
28. TESTER, D. A. and MOFFITT, T. W. Vinyl chloride monomer in food packaging. Paper given at the *BPF/PRI Joint Conference Vinyl Chloride and Safety at Work*, 28 May 1975.
29. GILBERT, S. G. 'The migration of minor constituents from food packaging materials.' *J. Food Sci.*, 41, 1976.
30. ABRAMOWITZ, R. J. 'Bulk polymerisation plants.' Paper given at the 172*nd ACS National Meeting*, San Francisco, 2 September 1976.
31. Unexamined Japanese Patent 47 076 (1976).
32. Unexamined Japanese Patent 47 081 (1976).
33. Unexamined Japanese Patent 17 950 (1976).
34. Unexamined Japanese Patent 17 287 (1976).
35. *Food and Cosmetics Toxicology*, 14, No. 5. (1976) 498.
36. *The Determination of Vinyl Chloride*. A Plant Manual published by the Chemical Industries Association, Alembic House, 93 Albert Embankment, London SE1 7TU.
37. *VC/PVC: Health Protection Measures*. Verband Kunstofferzeugende Industrie e V Frankfurt. 12 November 1974.
38. *Colloque Scientifique sur le Chlorure de Vinyle Monomère*, tenu le mardi 2 Mars 1976, à l'Institut du Radium Fondation Curie, Paris.

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