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ETHYL CORP. R & D DEPT.
BATON ROUGE
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U S A

Your ref	Our ref	Tel ext	Date
	GJS/CCB/DSO-320	3645	6 June 1974

Dear Al

We (in common with the rest of the world's PVC industry !) have been looking hard at ways and means of reducing the concentration of VCM in our 'Corvic' plants. We have recently talked in detail with Solvay about this problem and a joint document has been prepared summarising the work we have already done, or plan to do. A copy of this document is attached.

One point is perhaps worth making on the matter of tanker connections (Section 4.1). Although on our 'Corvic' plants the wearing of air masks during tanker off-loading is mandatory, our Mond Division colleagues hold the view that wearing air masks for normal operation is not necessary provided that both liquid and vapour equalising lines are provided as rigid pipework connections with swivel joints as a properly designed counter-balanced assembly; so that one can have either the specialist assembly or the air masks.

You will be interested, too, in the way in which ideas on standards are moving in the UK. At present the "good practice" TLV of 200 ppm is still operative, although all UK manufacturers are working to an average background VCM concentration in their plants of 50 ppm or lower. However, the Government is clearly thinking of an interim standard of 25 ppm average exposure with maximum exposure of 50 ppm, probably as a legal requirement in the next two or three months. This could, I expect, be followed by a further reduction depending on the way in which your own legislation goes.

Please let me know if you have any queries on the data attached (or indeed on the European vinyl chloride toxicity scene).

Kind regards

Yours sincerely

Guy Sleddon

G J Sleddon

Enc

EC 4393

IMPERIAL CHEMICAL INDUSTRIES LIMITED
PLASTICS DIVISION - WELWYN GARDEN CITY

VINYLS TECHNICAL CONTROL

PVC PLANTS : THE MEASUREMENT AND REDUCTION OF VINYL CHLORIDE LEVELS IN AIR

1. INTRODUCTION

The finding that vinyl chloride monomer (VCM) inhaled for long periods at a sufficiently high concentration can cause a rare form of liver cancer (angiosarcoma) in rats and mice, and the discovery of a number of cases of this disease amongst PVC autoclave operators early in 1974 has led to a general concern in the PVC manufacturing industry to reduce operator exposure to VCM vapour. Solvay and ICI have made an investigation of VCM concentrations in the atmosphere of their plants, and are carrying out a programme to reduce these concentrations and the exposure of their plant operators to them. This note is written to give Licensees guidance on the areas where there is a risk of potentially high VCM concentrations, and guidance on plant process changes to reduce VCM exposure.

2. STANDARDS

The realisation that there is an additional health hazard associated with VCM will clearly lead to a downward revision of the safe exposure limits, though at the moment there is insufficient knowledge for permanent standards to be set. The emergency standard currently adopted in the USA specifies that no employee shall be exposed to a concentration of VCM greater than 50ppm by volume in air. Sweden has adopted as a temporary standard an average threshold limit value (TLV) of 20ppm, with exposure to 50ppm allowed for periods up to 15 minutes. Solvay and ICI have been taking a TLV of 50ppm as being the best guidance on safe practice at the moment, though the achievement of significantly lower levels is a desirable target.

3. THE MEASUREMENT AND MONITORING OF VCM CONCENTRATIONS

This section presents a summary of analytical techniques, and an Appendix lists some sources of analytical equipment, suitable for the detection and measurement of VCM.

3.1 Laboratory Techniques

Laboratory analysis of air samples taken on the plant can be made by the techniques of flame ionisation, gas chromatography, or infra-red spectorscopy. The last two can be specific for VCM. Sampling and analysis are slow, and the use of laboratory measurement is unsuitable for the thorough survey and monitoring of plant atmospheres.

3.2 Mobile Equipment for Plant Monitoring

The most useful equipment found so far for this purpose is the Century Organic Vapour Analyser (OVA). This is a portable battery-operated flame ionisation instrument sensitive in the region 5-200ppm on one scale, and able to measure higher levels on an alternative scale. It is not specific for VCM, but this is not generally a serious limitation on a PVC plant because VCM is usually the major combustible vapour present.

The OVA has not been certified as intrinsically safe for use in an explosive VCM/air atmosphere, and hence some care must be exercised in its' use, though the design incorporates safety features which give considerable protection against the explosion hazard. Because the OVA gives a direct reading it is very valuable for quick atmospheric measurements and for leak location, which has now become a more important aspect of plant operation.

Infra-red analysers are sensitive and can be specific for VCM, but have the disadvantage of being heavy, not direct reading, and sometimes affected by vibration. They are generally not designed for use in an explosive atmosphere and have to be modified for this duty, or operated in a safe atmosphere. Two proven types are the Miran and the Unor.

3.3 Centralised Equipment for Plant Monitoring

It is likely that the installation of centralised, automatic, multi-point analysis systems will become standard practice in the autoclave buildings of PVC plants. Automatic sampling systems are available for monitoring up to 24 stations. Measurement of the VCM concentration may be by flame ionisation, by gas chromatography, by infra-red analysis, or by pyrolysis followed by absorption in water and conductiometric estimation of the chloride produced. Flame ionisation detection gives a sampling interval of 2 minutes, compared with 6 minutes for gas chromatography, and hence is to be generally preferred when vinyl chloride is the only organic vapour present. The Bendix Corporation make a 24-point continuous analyser of this type. Equipment for the pyrolysis/conductivity technique, as used by the Dow Chemical Company, is made by AED Inc of Chicago.

3.4 Equipment for Personal Monitoring

The Casella personal monitor is sufficiently light to be carried by an operator during his work, and can be used to give an average measure of VCM exposure. The equipment draws air through activated charcoal at a constant rate for a known time, possibly up to 8 hours. The VCM is subsequently dissolved in dichloromethane and measured by standard gas chromatographic techniques. The equipment may also be used to obtain time-average concentrations for selected plant locations. The Casella has proved useful as a check against TLV values calculated from measurements of VCM at work locations and the operator's work schedule. Because the Casella does not give an immediate result there is no warning of an approach to the safe exposure limit.

4. THE REDUCTION OF VCM LEVELS IN THE PLANT ATMOSPHERE

The autoclave stage of the process is the cirtical one from the point of view of exposure to VCM. This comes from emission to the plant atmosphere when autoclaves are opened for cleaning and through leaks at joints, seals, and valves. Operator exposure may be high when working inside autoclaves and particular precautions are then necessary. Hence a substantial part of the effort to reduce VCM concentrations has to be on the autoclave stage of the process. Other parts of a PVC plant which can give high local VCM concentrations at operator working points are filters, stock tanks, and centrifuges. Enclosed drains may contain high levels of VCM if there is little air movement within them, even where the VCM concentration in the liquid effluent is low, due to the limited solubility of VCM in water. The following types of action can be taken to reduce VCM concentrations and operator exposure to these:-

1. Modification of operating procedures, using existing plant, to reduce VCM emission to the plant atmosphere.

2. Increased personal protection. For example the use of fresh air masks when there is a risk of exposure to high VCM concentrations.

3. A higher standard of maintenance on equipment containing VCM under pressure, requiring a schedule of detection and prompt action to stop any leak.

4. Plant modification either to the process equipment or to the building containing it. For example the provision of local extraction systems at key points, and a general increase in the frequency of air change in the autoclave building.

When designing or carrying out modifications to plant procedures or equipment to reduce exposure to VCM for toxicity reasons it is essential to make sure that the explosion hazard is still adequately covered.

The main process steps are considered in more detail below.

4.1 Monomer Handling

There is a danger of leaks and spillage when unloading VCM road or rail tankers and it is desirable that the operator should use a fresh air mask for this operation. Pipework taking VCM should have as few joints and valves as possible. VCM transfer pumps, weigh vessels, post- and ante-vacuum pumps are particular sources of leaks and should be sited outside the plant building or provided with local ventilation.

4.2 Autoclaves and Strippers

The adequate ventilation of polymerisation buildings is important, with about 15 air changes an hour likely to be desirable in the working areas, achieved either by forced air flow or by opening the plant to increased natural ventilation. Precautions should be taken to direct the flow of air and to prevent the accumulation of dense VCM vapour. In the event of a major VCM leak a high rate of air change in an enclosed building will accelerate the mixing of VCM and air to give a larger volume of gas within the explosive composition range that would otherwise occur. This could make the escape of operators from the danger zone more difficult, and will increase the violence of an explosion should one occur. For this reason there should be means of turning off any large forced ventilation system in an emergency.

The air for pressurised control rooms should come from a source where the VCM concentration is always low.

The following steps can be taken to reduce VCM emission directly associated with the autoclaves and strippers, to reduce the exposure of autoclave operators, and also to lower VCM levels at later stages in the process:-

1. Ensure good performance of the post-vacuum system in order to remove as much VCM as possible to the VCM recovery plant.

2. Ensure good operation during stripping of slurry or latex, because this will reduce the degree of VCM emission from subsequent filters, stock tanks and in the drying section.

3. Following the usual post-evacuation, the breaking of the vacuum to atmospheric pressure with nitrogen followed by a further evacuation through the ante-vacuum system would reduce the residual VCM in the autoclave and so reduce the quantity which might escape into the plant atmosphere. If this second evacuation step is adopted nitrogen should be used to eliminate the risk of explosive gas mixtures in the ante-vacuum system.

4. Escape of VCM following lid removal can be a major source of VCM in the general plant atmosphere. As soon as the manhole is opened apply suction through the ante-vacuum system to maintain an inward flow of air at the manhole to prevent the escape of VCM into the working area. The extraction exit should be outside the building. Care must be taken that the gas mixture going through the ante-vacuum system is below the lower explosive limit.

   To avoid interference with the normal duty of the ante-vacuum system it may be desirable to increase pump capacity or install an additional extraction system.

5. Following hydrodynamic cleaning, the autoclave should be thoroughly purged with fresh air. This may be done with a fresh air sleeve, with the exit air taken outside the autoclave building, either through the ante-vacuum system or other pipework, and not blown into the working area. It may be possible to fit a compressed air Venturi ejector to the autoclave run-off system so as to achieve a high rate of air change within the autoclave. An additional precaution which can be taken if entry into the autoclave is required, is to fill the autoclave with water while continuing to run the ante-vacuum system, so displacing the VCM vapour through the vacuum system.

4.3 Run-down Systems and Filters

Cleaning and maintenance on enclosed filters should be done using a fresh air mask. Open filters can be a source of high operator exposure during the removal of coarse material, particularly when this is done during the run-down of the batch. Ventilation hoods can be fitted, these being open at the operator position only. If the filter is inside a building the ventilation exit should be outside the building.

4.4 Stock Tanks

Relatively high levels of VCM can build up in the air space of a stock tank, and then displaced into working areas by natural air currents and the rise in the stock tank liquid level when a batch is discharged. An air ventilation system can be used to take this evolved VCM away from working areas.

4.5 Centrifuges, Driers, Screens and Packing

Centrifuges and immediately associated equipment are the only major source of VCM in the atmosphere of the drying building. Improvements can be made by installing a local extraction system, and by opening the building to natural ventilation. Only low VCM concentrations have been found near screens and sack packing equipment. Vent points in air conveying systems may need to be ducted outside the plant building.

4.6 Polymer Storage

Dried PVC contains a low residual level of VCM. When stored in sacks VCM escapes slowly leading to a level in the store atmosphere which depends on ventilation, the amount of material in the store, and the temperature. It will generally not be difficult to provide sufficient ventilation to maintain levels below 50ppm in the atmosphere. In silos, which are not usually ventilated, higher concentrations can develop and entry should only be made after purging the atmosphere, or when wearing suitable breathing apparatus.

4.7 PVC Waste

Dried PVC waste does not present a hazard, but wet waste can contain a relatively high level of VCM and should be stored outside rather than inside plant buildings.

5. ENVIRONMENTAL ASPECTS OF VCM EMISSION FROM PVC PLANTS

The emission of VCM to the environment is very largely through gaseous streams, approximately half being in the drier exhaust gases and the remainder distributed over a number of sources. The latter are particularly the autoclaves, VCM recovery plant, and stock tanks.

VCM is known to react rapidly with ozone. A half-life of a few weeks has been estimated under atmospheric conditions due to reaction with the naturally occurring level of ozone. Hence VCM will not accumulate in the atmosphere.

P P MANNING

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APPENDIX

Analytical Equipment Manufacturers

Further information on the analytical equipment mentioned in this note is available from the following suppliers:-

1. Century Organic Vapour Analyser (OVA)

   Century Electronics & Instruments Inc, 6450 E. Apache, Tulsa, Oklahoma 74115, USA.

2. Miran infra-red analyser

   Wilkes Scientific Corp, South Norwalk, Connecticut 06856, USA.

3. Unor infra-red detector

   H Maihak AG, Semperstrasse 38, 2000 Hamburg 39, W. Germany.

4. Bendix 24-point flame ionisation monitor

   Bendix Corp, Process Instruments Division, PO Drawer 477, Ronceverte, W. Virginia 24970, USA.

5. Dow Company pyrolysis/conductiometric method

   AED Inc, 1913 W. Irving Park Road, Chicago, Illinois 60613, USA.

6. Casella personal monitor

   C F Casella & Co Ltd, Regent House, Brittania Walk, London N1 7ND, UK.

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