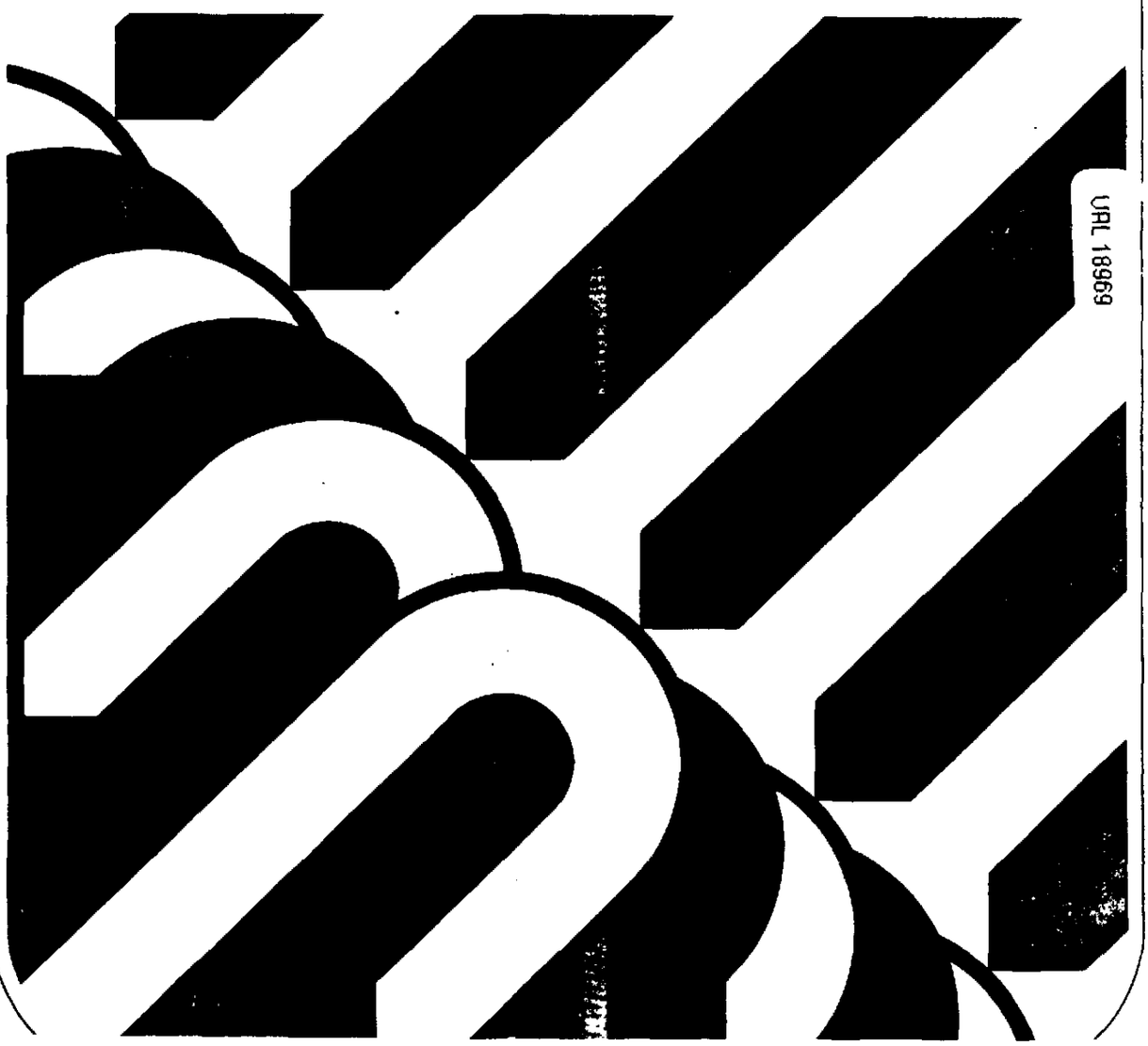
VC/PVC: An Example of a Problem Resolved



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Contents

Less than a year has elapsed since we presented the information available at the time on the symptoms of disease that had been associated with vinyl chloride (VC) - the basic material for polyvinyl chloride (PVC). We closed our publication "VC/PVC: Reasons for Health Protection" by improving the hope that we will be successful in further developing the production processes within a reasonable period of time so that a hazard to health can be excluded.

To call this in doubt appeared presumptious to many, since the PVC manufacturers themselves had required their development departments to ensure medical safety at the working site, air pollution prevention, protection of the work area and consumer protection.

Whilst the PVC processing industry has made extensive efforts to further improve health protection in its sphere of activity, the PVC manufacturers in the Federal Republic of Germany have, at considerable expense, developed completely new technologies of PVC production within an extraordinarily short time.

A technical solution to the problem has been found. Translating it into practice is being realized and has in part been completed.

The results which have been achieved with considerable effort are an example of how a problem was solved because all concerned cooperated wholeheartedly and energetically: factories and their employees, federations of industry, supervisory bodies, ministries, science and the PVC manufacturing and processing industries.

An attempt here and there to create adverse publicity and to make political capital out of reports on illnesses seems to be an accompaniment which one

has to accept. However, legislators and supervisory bodies in the Federal Republic of Germany have given preference to a responsible analysis of the risks involved, weighing all positive and negative aspects, rather than taking decisions entirely on political grounds. Their action has been borne out by an industry which has shown a high sense of responsibiliy.

It will be possible to meet all deadlines set for the coming into force of new safety conditions and in some cases even to bring these deadlines forward. PVC processing will not involve any hazards to health through VC and the consumer will be supplied with food packings and other PVC products which ensure an even higher measure of health protection than hitherto.

Frankfurt am Main, 15th September 1975

"No human activity, job or habit is without some risk, and we should avoid setting up rules or opinions which would only serve to exchange one kind of hazard for another of possibly greater dimension."

(Independent Norwegian Medical Commission for the resumption of PVC production at Norsk Hydro; 16th December 1974).

PVC as an Economic Factor

PVC, the first fully synthetic plastic, has been produced on an industrial scale for over 40 years. At an annual production in 1974 of 1.0376 million tonnes PVC takes second place after polyethylene in the Federal Republic of Germany.

Applications

Because this plastic can be especially well tailored to the properties required in a given application, there are many different possible uses. Articles of great diversity can be made from PVC, for example, gramophone records and cable insulations, underseals for automobiles, liquid plastics for basement floor coverings and artificial leather, facade elements and roof liners for motor cars, roof guttering and hoses, pipes and window frames, clear bottles and floor coverings, floating toy animals and shower curtains, margarine tubs and conveyor belts.

In addition, its protective action against aggressive media and corrosion raise PVC to the level of a modern material which contributes towards surmounting acute environmental problems.

Thus PVC is not just any versatile raw material; if this were all, it could simply be prohibited if it disturbs us and our environment, and the problem would be solved.

Economic Significance

On the contrary, PVC - viewed worldwide - is the biggest large-tonnage plastic whose sales value in the form of the raw material is DM 16.000 million per year. But this demonstrates its economic significance in outline only. Its real importance only becomes evident if besides the quantity and value of the articles made from it one also considers the starting products and associated production fields, auxiliaries, machines, die construction, as well as processing, fabrication and its use in all branches of industry. Stated in simple terms, this means tens of thousands of jobs, capital expenditures worth thousands of millions, decades of research and development, a chain of economic and technical interrelations and not least a material-dependent standard of living.

PVC Products in the Federal Republic of Germany, 1974

	%
Panels, film and sheeting (plasticized and unplasticized)	23
Pipes and fittings	23
Rigid profiles (incl. roller blind slats)	16
Cable sheathings	9
Floor coverings	8
Coated fabrics	8
Hoses and soft profiles	4
Blow moulded articles	3
Others (incl. gramophone records, shoes, balls)	6

PVC as an Economic Factor in the Federal Republic of Germany, 1974

	Jobs	Sales Factory Prices DM million	Invested capital DM million
Vinyl chloride and PVC production	6500	2040	1900
- production sectors of the chemical industry directly associated	8600	1700	3100
Auxiliaries and additives	1800	440	310
Processing machines	4300	320	-
Semi-finished and finished products	42800	4020	3710

PVC Applications in the Federal Republic of Germany, 1974

Building and engineering industry	55 %
Packing industry	13 %
Vehicle construction, transport	6 %
Office equipment	5 %
Furniture manufacture	4 %
Electrical industry	4 %
among others, agriculture, measuring and control instruments, machinery manufacture, games and sports	13 %

In the Federal Republic of Germany alone over 60.000 people and their families currently owe their living to PVC. In 1974 they produced goods worth more than DM 4.000 million. Over DM 9.000 million has been invested in their jobs.

The products of the plastics processing industry go into numerous fields of application and use where, for economic and technological reasons, one could no longer manage without PVC.

Linked Chemical System

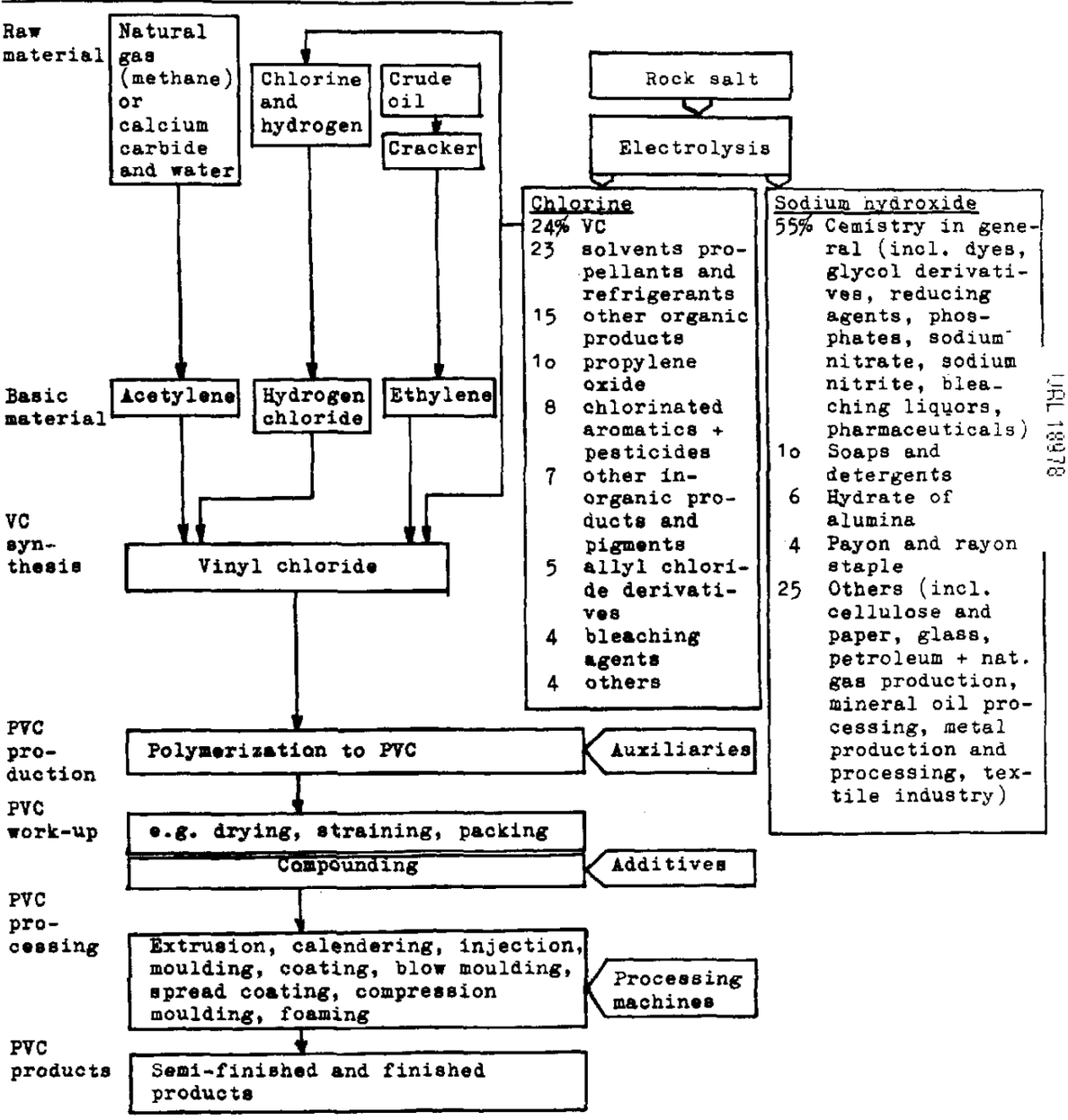
PVC is made from vinyl chloride (VC) gas. VC is obtained either from acetylene and hydrogen chloride or from ethylene and chlorine. Chlorine is thus always involved - and chlorine is more of an awkward chemical. In the electrolysis of rock salt it is formed alongside sodium hydroxide as an unavoidable joint product, in the unalterable ratio of 10 to 11. For most basic chemical processes, sodium hydroxide is an indispensable substance. Among other things, the manufacture of many pharmaceuticals and dyes, of aluminium, textiles, glass and paper are dependent on it. The problematic twin of sodium hydroxide, the aggressive, highly toxic chlorine gas, is used directly for the manufacture of solvents, propellants and refrigerants, propylene oxide, bleaching agents and other products. The largest field of application accounting for nearly one quarter of the consumption of chlorine is the production of vinyl chloride and consequently PVC.

In the production of sodium hydroxide from rock salt one must accept approximately the same amount of chlorine. That is why the development of the sodium hydroxide-consuming industries is linked directly with the development of chlorine-consuming products. If one could no longer convert the chlorine into VC, one would have to cut its production by 24 % because the other uses are hardly capable of further development. At the same time, however, 24 % less sodium hydroxide would be produced and a corresponding raw material gap of all sodium hydroxide-dependent products would result.

Thus PVC, quite apart from its economic and technical importance, plays a key role in the maintenance of the equilibrium in the linked system of the chemical industry.

In addition, by binding the problematical basic chemical chlorine already in the manufacturing stage, it helps in avoiding structural environmental damage.

Production of PVC and Linked Chemical System



Problems of Industrial Medicine

Vinyl chloride is a colourless gas and can be smelt only in higher concentrations. For decades it was considered a harmless halogenated hydrocarbon. The "Pocket Dictionary of Industrial Medicine" published in 1966 still claims that vinyl chloride does not damage the liver, kidneys, central nervous system or bone marrow. The standard work entitled "Chemistry and Toxicology of Plastics" published in 1966 by Lefaux reads: "Vinyl chloride is a gas of relatively low toxicity. At higher concentrations it has a slightly narcotic effect and irritates the eyes".

First Pointers

In 1949, Soviet researchers reported on liver damage detected in 15 workers exposed to VC. The Romanian, Suciu, remarked with reference to this as late as 1963, that transient toxic inflammation of the liver must have been concerned. These observations made in the Soviet Union and Romania remained unnoticed in the west for a long time, as they were inacessible and are still not available in detail. It was as late as 1968 that Schottek, in a lecture held in Leipzig, came to the conclusion that liver and kidney damage was caused by chronic exposure to VC.

In the meantime the attention of researchers in the west had been drawn to this problem. When injury to the health of cleaners of polymerization reactors[1]) had been reported for the first time in the mid-sixties, the opinion on the innocuousness of VC gas held in western Europe changed. The injuries to health manifested themselves in many different ways, i.e. as bandlike bone defects on the terminal ossicles of the fingers (acroosteolysis) and as blood flow disturbances in the hands, as well as "pins-and-needles" and abnormal sensitivity to cold (Raynaud's syndrome). In addition, platelike hardening of the connective tissue, mainly of the forearms (sclerodermia) was detected. The findings were published in 1966 and interpreted as manifestations of occupationally induced disease.

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1) Polymerization reactors are pressure vessels in which vinyl chloride is polymerized to PVC

In the Federal Republic of Germany, acroosteolysis and Raynaud's disease were observed for the first time in 1972.

Reduction of the Threshold Limit Value

In 1966 the VC concentration in the work area of the German PVC production plants was fixed at 500 ppm[1]) by TLV[2]) regulation.

According to the definition of the Kommission zur Prüfung gesundheitsschädlicher Arbeitsstoffe der Deutschen Forschungsgesellschaft (Committee of the German Research Association for testing injurious working materials) the TLV is that concentration of a working substance in the form of gas, vapour or suspended matter in the ambient air of the work area which according to the present state of our knowledge does not impair the health of the employees exposed repeatedly and over prolonged periods, as a rule for 8 hours a day, during an average working week not exceeding 45 hours. In 1970 the TLV was reduced to 100 ppm, following the outcome of animal experiments in which liver changes had been noted as a result of exposure to VC. The new TLV was so low that further disease seemed impossible. Consequently there did not appear to be any grounds for conducting further research.

The So-called VC Disease

Whilst it was originally supposed that the cause of the initially detected injuries were due to the direct contact of the skin with VC-containing PVC (which was formerly scraped off manually from the wall of the polymerization reactor), subsequent observations, above all of liver damage, demonstrated that inhalation of VC-containing air must also be dangerous.

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1) ppm = parts per million

2) TLV = threshold limit value

Today we know more and can better interpret the observations of widely differing symptoms which were noted at various times in different locations, and piece them together to form an overall picture. Thus also the observations published in 1973 by Professor Veltmann and his co-workers (University Skin Clinic, Bonn) which they had made since 1972 with respect to the workers of a near-by PVC plant. They found that VC, besides causing the already well-known damage to the bones and skin also impairs the blood picture, the liver and spleen. They drew the conclusion that the so-called VC disease was systemic in nature.

The first pointers to the weightiest complex of the disease symptoms, the incidence of cancer in connection with exposure to VC, was provided by Professor Viola (Solvay) in Tokyo in 1969. He had detected numerous carcinomas in rats exposed to VC. His investigations, however, had been conducted with dosages which at 30.000 ppm were near the explosive limit of the VC-air mixture.

As these dosages were in no way comparable to the VC concentrations occurring in work areas, Professor Maltoni of the Instituto di Oncologia, Bologna, was commissioned by ICI, Montedison, Rhone-Progil and Solvay to check Viola's findings under conditions more in line with practice. In December 1973 he detected liver angiosarcomas, a rare form of cancer of the liver, in rats exposed for up to one year to VC concentrations of 250, 200 and 50 ppm in the ambient air.

A little later, in January 1974, liver angiosarcomas, previously only detected in animal experiment, were diagnosed in workers of PVC production plants in the United States of America. Subsequently, on 22nd May 1974, a value of 50 ppm was fixed[1]) by the Bundesministerium für Arbeit und Sozialordnung (Federal Ministry for Labour and Social Affairs) as the limit for the VC concentration in work areas, as had been proposed by the Berufsgenossenschaft der Chemischen Industrie (Professional Liability Insurance Association of the Chemical Industry); the TLV regulation for vinyl chloride was discontinued soon afterwards. As a rule this is done with substances which have proved carcinogenic in man or only "in animal experiment under conditions comparable to the possible exposure of human beings in the course of their work."

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1) "Arbeitsschutz" No. 6/1974, p. 196

If the TLV regulation for a substance is rescinded, a so-called technical guiding concentration that takes into account the technical possibilities may take its place. A technical guiding concentration of 5 ppm as an annual average has been fixed jointly by the representatives of the authorities, the Professional Liability Insurance Association of the Chemical Industry, scientists and the plastics industry.

Diagnostic Problems

At the same time extensive and intensive studies on the state of health of workers in VC and PVC producing plants were launched throughout the world. In addition, a start was made of checking all employees, on the basis of new knowledge, as to earlier illnesses which might be connected with VC. It was still only possible to detect only the pathological symptoms, but not to determine precisely the cause, extent and effects, although more than 550 scientific publications had appeared meanwhile.

The special problem of all these examinations lies in the fact that the individual symptoms of all pathological manifestations brought into connection with VC are not in themselves specific to VC. Thus, for example, acroosteolysis, Raynaud's syndrome, sclerodermias and thrombocyte changes have always occurred in the average population, in part quite frequently, also without exposure to VC.

The thrombocyte count of a person can fluctuate considerably within a very short time. Wrong diagnoses are readily made if one relies on the symptom alone.

The changes in the liver of VC workers are very specific disturbances - so-called fibroses of the liver which can only be recognized as such by means of microscopic tissue examination of the liver.

Demarcation of VC-induced changes of the liver from the more frequent other cases of liver damage provides special difficulties for diagnostics, as the usual laboratory methods are not suitable. A diagnosis can only be made in specially equipped clinics. This applies above all to the most serious affection, i.e. angiosarcoma which can only be definitely diagnosed by means of histologic tissue examinations using radioactive substances. This involves a surgical procedure in each instance and prolonged hospitalization. For this reason such tests have to be restricted to suspected cases detected in mass examinations.

Research

The discussion as to how the individual pathological symptoms come about has not ended. But there is hardly any doubt that they are ascribable to contact with VC. We still know too little about the mechanism of action of VC. Nor is it known in how far other influences simultaneously play a part. Extensive research that is still in progress is intended to clarify these questions; it is being conducted at the Institute for Toxicology and Pharmacology of Würzburg University, the Central Institute for Industrial Medicine of Hamburg University and the Medical Inspectorate of Factories, North-Rhine District.

Until these studies have been completed it will not be possible to fix threshold limit values (TLV) that are based on toxicological data established under principles of industrial hygiene. Consequently the lowest possible concentration of vinyl chloride in the respiratory air must be aimed at by means of continued improvement of the technical factors.

Statistic of the Cases of Disease

Considerable attention is given to this problem in all industrialized countries. Besides clarifying the mechanism of action, one is endeavouring to record as completely as possible all cases of disease and death due to VC.

Unfortunately only scant information is available from eastern countries. Of the 42 fatal cases of hemangiosarcoma of the liver, two were reported from Czechoslovakia and one from Romania. No other fatalities are known from other Socialists Countries. Twenty cases of acroosteolysis, sclerodermia, disturbances of pulmonary function and thrombocytopenia have been detected in Poland.

Until July 1975 a total of 222 suspected cases of VC desease were reported in the Federal Republic of Germany to the respective Professional Liability Insurance Associations, including six resulting in death. These fatalities were in respect of the VC/PVC manufacturing industry; the diagnosis was angiosarcoma of the liver. Three of these cases have now been acknowledged as occupational disease by virtue of a notice to the effect that a pension had been granted.

Of the remaining 216 cases reported, 151 came from PVC production and 65 from PVC processing.

It should be noted in this connection that a doctor who has grounds for suspicion that a worker has contracted an occupational disease, must report this under Articles 5 & 7 of the Occupational Diseases Ordinance to the responsible body of the statutory accident insurance (Professional Liability Insurance Associations), as well as the government agency responsible for industrial hygiene (medical inspectorate of factories).

The cases reported include 70 without findings stated; they were apparently filed as a precaution. This probably explains the relatively high proportion of cases in which no impairment of the capacity to work occurred: of 88 cases from PVC production finally appraised in the meantime, 55 have been rejected. Suspected cases from plastics processing have not yet been confirmed anywhere in the world.

It may be premised that following observance of the concentrations for VC in the work area currently applicable in the Federal Republic of Germany, no new cases of injury to health will occur. The fact that cases of illness did occur, is attributable to the lack of knowledge about the true danger of vinyl chloride and the high VC exposure of employees this occasioned.

Dangers due to VC

According to the present state of our knowledge the substance dangerous to man is vinyl chloride alone. For this reason appropriate safety measures have to be taken already during its manufacture.

In the production of VC and PVC a certain proportion of the vinyl chloride is lost owing to its high volatility and escapes into the atmosphere (emission); in the past, depending on the manufacturing process employed, this was up to 5 %.

Traces of VC contained in the waste water of the manufacturing plant quickly escape into the atmosphere owing to the VC's low solubility in water, so that the waste water is virtually free of VC while still within the factory boundary.

The volatile VC gas is rapidly distributed in the atmosphere. At a distance of several hundred meters from the sites of emission, ambient air concentrations of less than 1 ppm have been detected in the past. With increasing distance the concentration quickly drops below the limit of detection. No injury to people living in the vicinity has been detected to date anywhere in the world.

As with other products in powder form the occurrence of dust is not completely avoidable in the manufacture and processing of PVC. In any event, for reasons of industrial hygiene, the TLV for inert[1]) dusts of 8 mg/m^3 must be conformed to or must fall short of this value, by instituting suitable measures. Where this concentration has been observed, no damage has been recorded in the past.

Because the finished PVC powder still contains certain residual amounts of VC, down-stream processing stages may be affected by these problems, albeit to a considerably lesser extent.

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1) "Dusts and fumes which according to the present state of our knowledge neither have a toxic or fibrogenic effect and produce no specific pathological symptoms" are considered inert by the TLV Committee of the German Research Association

Development of new Technologies

PVC is produced on an industrial scale by three different processes:

emulsion polymerization
suspension polymerization
bulk polymerization

The starting material for the manufacture of PVC is vinly chloride. It is polymerized to PVC at a VC vapour pressure of about 6 to 16 bar at temperatures between 40° and 80° C. At atmospheric pressure vinly chloride boils at -13.8° C and dissolves in large quantities in the PVC during polymerization. As polymerization progresses these dissolved amounts are also largely converted into PVC.
The speed of every chemical reaction is dependent on the concentration of the substances taking part. Consequently polymerization of the PVC slows down towards the end of the reaction, because the concentration of the VC monomer in the reaction mass drops continuously. Theoretically one would therefore have to wait indefinitely for the final residue of VC to be polymerized. The reaction is stopped, depending on the process employed, when about 90 % of the VC has polymerized. The time of stopping the reaction is important for the properties desired and required for the subsequent processes. In all processes the reaction is stopped by pumping the remaining VC gas out of the polymerization reactor; it is subsequently recovered by liquefaction and recycled to the production process.

Work-up stages follow the polymerization reaction. They comprise mainly drying, straining, transfer within the works, and packing.

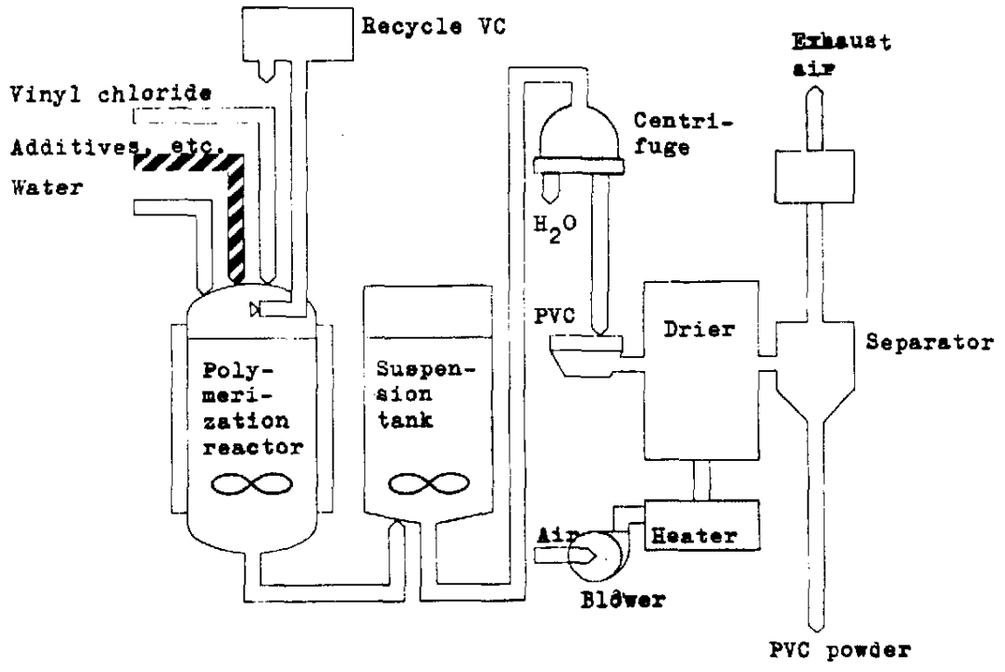
Industrial Safety

Owing to the fact that VC is usually produced in open-air plants, leakages in the plant system cannot result in higher VC concentrations in the air of the work area because of the favourable diluting effect.

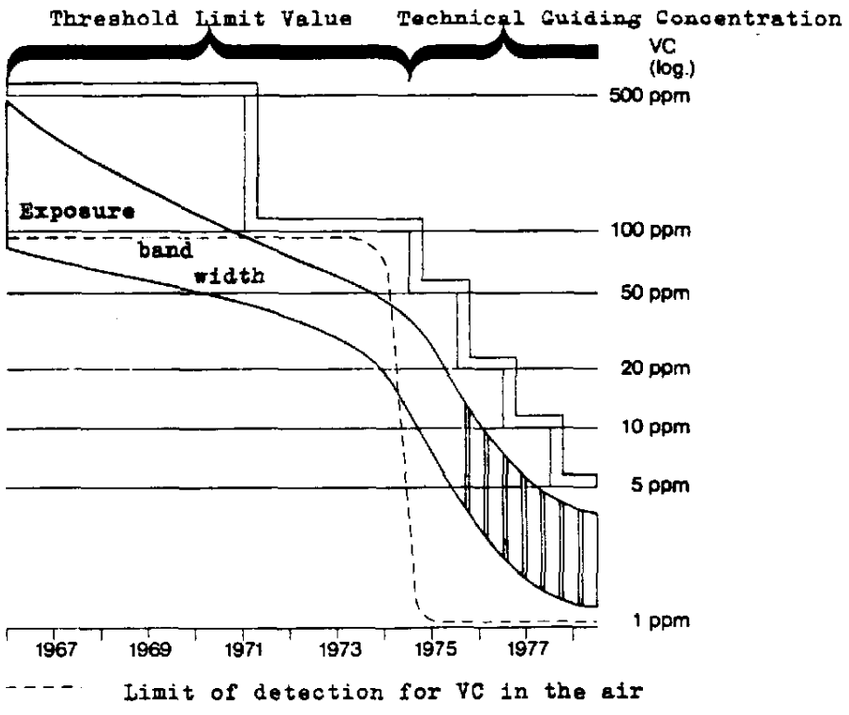
The situation is different as regards the polymerization of VC and the subsequent work-up of the PVC which is done mainly in closed rooms.

Additional problems arise for industrial safety because PVC production must largely be carried out in intermittent operation. The polymerization reactor has to be opened and closed again and again, filled and emptied, cleaned and regulated. These changing loads on valves, flanges, shaft openings, control instrument fittings and the manipulations this requires, result in wear and finally in leakages.

Production of Suspension PVC



Development of the VC Concentration in the Work Area in PVC Production in the Federal Republic of Germany



So long as one could assume with a clear conscience that VC was a relatively harmless chemical and a TLV of 500 ppm (high from the present point of view) was consequently fixed, the numerous small sources of VC were not known, nor were they of any special interest. On opening the polymerization reactors for cleaning purposes, the atmosphere they contained used to enter the ambient air unhindered. Consequently the highest VC concentrations were encountered in the work area of the PVC production plants. In the nineteen-fifties these concentrations probably amounted to several hundred ppm, occasionally even more. During manual cleaning of the polymerization reactors the workers were often exposed to more than 1,000 ppm VC in the ambient air.

Only when the danger of VC had been recognized, and the sensitivity of the measuring methods had been improved by several powers of ten, was it possible to trace these sources of emission and to take measures by which to remain under the limiting value for VC which had initially been drastically reduced to 50 ppm in 1974.

The fact that a possible risk particularly of cancer became known, required a rapid solution to the problem, regardless of scientific proof of the connection between exposure to VC and the so-called VC disease. For this reason the PVC-producing industry instituted many immediate measures by which to lower as far as possible the VC concentration in the work area. Only a few of these will be mentioned here, viz. the increased use of respirators, the considerably improved ventilation and evacuation of exhaust air from the manufacturing plants, extensive systems for exhaustion and leak-proofing, as well as avoidance as far as possible of manual cleaning of polymerization reactors by the use of automatic cleaning devices, and measures to reduce skin build-up in the reactors. However, intensified exchange of air in endangered work areas results in increased VC emissions if the exhaust air is not cleaned. In parallel with this, a start was made to subject the plants to a fundamental check for the possible escape of VC and to institute counter-measures. Extraordinarily difficult and expensive measures are required in the main for this purpose which in part, on the basis of VC leakage test results, necessitate the complete exchange of instruments, sealing elements and entire units of the plant, in connection with alterations to the process; such changes can therefore only be effected over prolonged periods. The German VC/PVC producers are spending about DM 100 million on these measures.

Although these measures are not quite complete, the VC content of the ambient air in existing PVC manufacturing plants already falls distinctly short of the demanded concentration of 20 ppm.

The technical guiding concentration, too, amounting to only 10 ppm, which comes into force on 1st July 1976, will certainly be reached by this date or even before, and the PVC manufacturers are making the greatest possible efforts to reduce the VC concentration even further in the work area.

Emission and Ambient Air Concentration

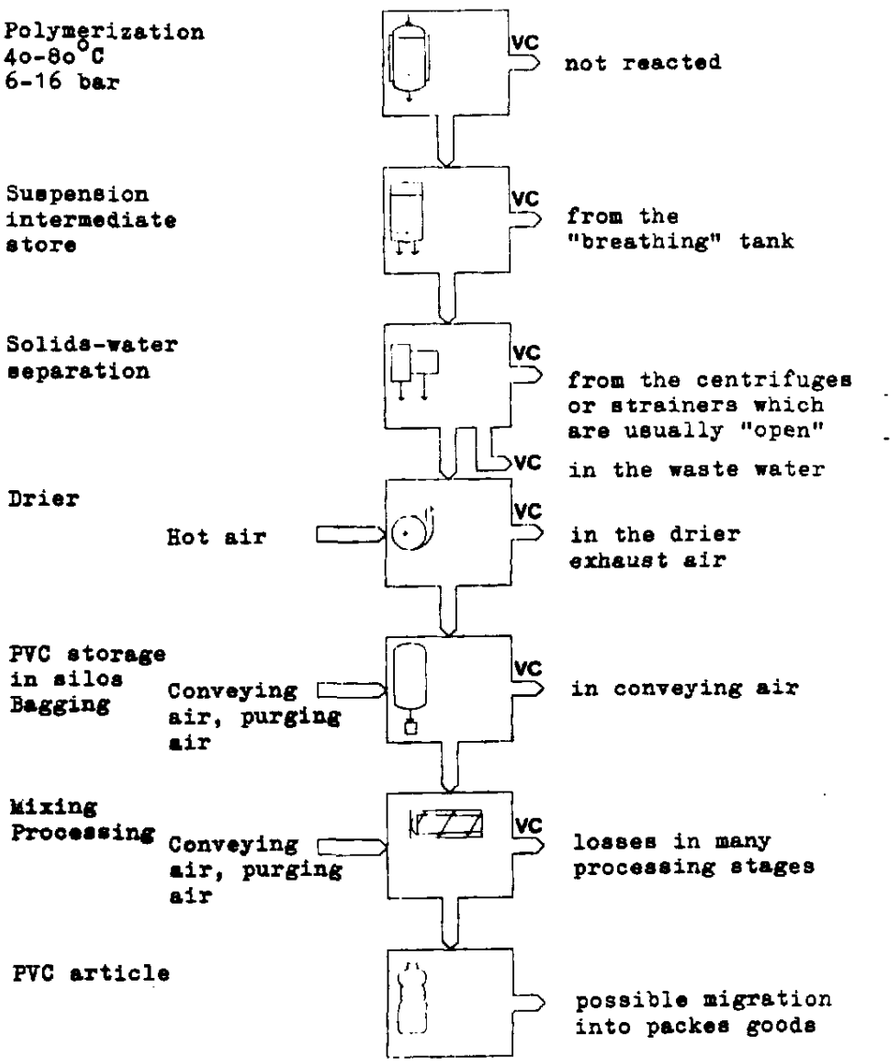
Although, if only for economic reasons, the greatest possible recovery of the VC not reacted in the polymerization process was aimed at, the emission of VC was unavoidable in some of the processing stages of PVC manufacture. This was the case mainly in the following operations:

ventilation of the polymerization reactor
ventilation of the intermediate storage tanks
exhaust air of the drier installations
inert gas discharge during reliquefaction of recovered VC.

The PVC leaving the reactor still contained substantial amounts of VC which were to a large extent liberated in the subsequent work-up operations. Only the residual VC pumped directly out of the polymerization reactor was returned to the production process. The TA-Luft (Technical Regulation for the Prevention of Air Pollution) passed in the autumn of 1974 stipulates a VC at all points which is smaller than or at most equal to 150 mg per m^3 off-gas if more than 3kg/h VC is emitted. These provisions exceeded by far the state of technology, both nationally and internationally. When the TA-Luft was passed, the actual VC concentrations in the most important sources of emission were still in the region of several thousand milligrams per m^3 exhaust air. At that time only laboratory and pilot plant know-how pointed to possibilities of reducing them.

Intensive work towards the solution of this problem has continued. It has not been possible by the further development of various exhaust air cleaning processes to reduce to any great extent the amounts of VC vented into the atmosphere. On the other hand the numerous off-gas streams and the large amounts of exhaust air made it seem illusory to fulfil the TA-Luft specification.However, it is possible by means of changes in the production process to further reduce the VC emissions as well as the concentrations in the work area. Trial runs of individual plants already converted permit the statement that it will be possible in the foreseeable future to achieve the emission limit values demanded. However, it will be necessary in all instances to effect extensive rebuilding on the existing plants.

Example VC Emieeion



Residual VC in the PVC

Until recently, a number of the PVC powder grades produced by the suspension and bulk polymerization processes contained over 1,000 ppm residual, unreacted VC. Despite degassing after polymerization and despite high temperatures during drying it was not possible to remove the residual VC from the PVC. This residual VC is partly liberated during storage and during subsequent processing. Consequently increased concentrations in the work area could not be ruled out.

Therefore, the thing to do was to reduce the residual VC content drastically, as well as the concentration in the work area and the emissions during PVC production.

The residual VC content in the PVC is determined by the following factors: diffusion path length, pressure and temperature.

To obtain an influence on the time factor, the degassing times employed hitherto would have to be extended very substantially, to several days or weeks. Apart from the storage problems this would entail, a longer residence time in driers or degassing plants at the temperatures employed in the past would damage the PVC owing to thermal degradation. In contrast, reducing the temperature during the degassing process would mean a further extension of the time required. Moreover, it would be necessary first to build such degassing plants.

This can therefore not be an adequate method by which to solve the problem.

How much VC migrates out of the PVC under otherwise equal conditions depends on grain size and grain density which determine the diffusion path length.

The larger the grain, the less gas will escape; the more porous the grain, the greater the degree of degassing. It would be possible to produce PVC which hat the most favourable grain properties with respect to degassing, but certain processing techniques and a large number of applications would have to be dispensed with. On the other hand PVC grades from the finest grain to coarse grain and from highly porous to glasslike are required in practice.

The degassing of PVC is favoured by high temperatures, too. However, the thermal stability of PVC is a limiting factor here. The addition of stabilizers at this stage is feasible but not expedient because the application spectrum of the material would be restricted.

By utilizing this knowledge and combining the aforementioned factors up to the load limit of PVC in each case under widely varying conditions, it has been possible to solve this problem to a great extent. By adopting a completely new mode of operation, decisive improvements in industrial safety and reductions in the VC emissions were simultaneously attained.

The Solution: Intensive Degassing

The incomplete recovery of the vinyl chloride dissolved in the PVC is the real cause of the subsequent chain of sources of emission in the areas of intermediate storage, work-up, drying, transport, storage and processing.

The problem to be solved consisted in that

- an atmosphere largely free of VC is necessary in the work area
- exhaustion, and consequently emission of the VC liberated at many points in the production operations is limited by statutory regulations, but
- complete avoidance of VC liberation is technically impossible and
- the final product supplied should be largely free of VC.

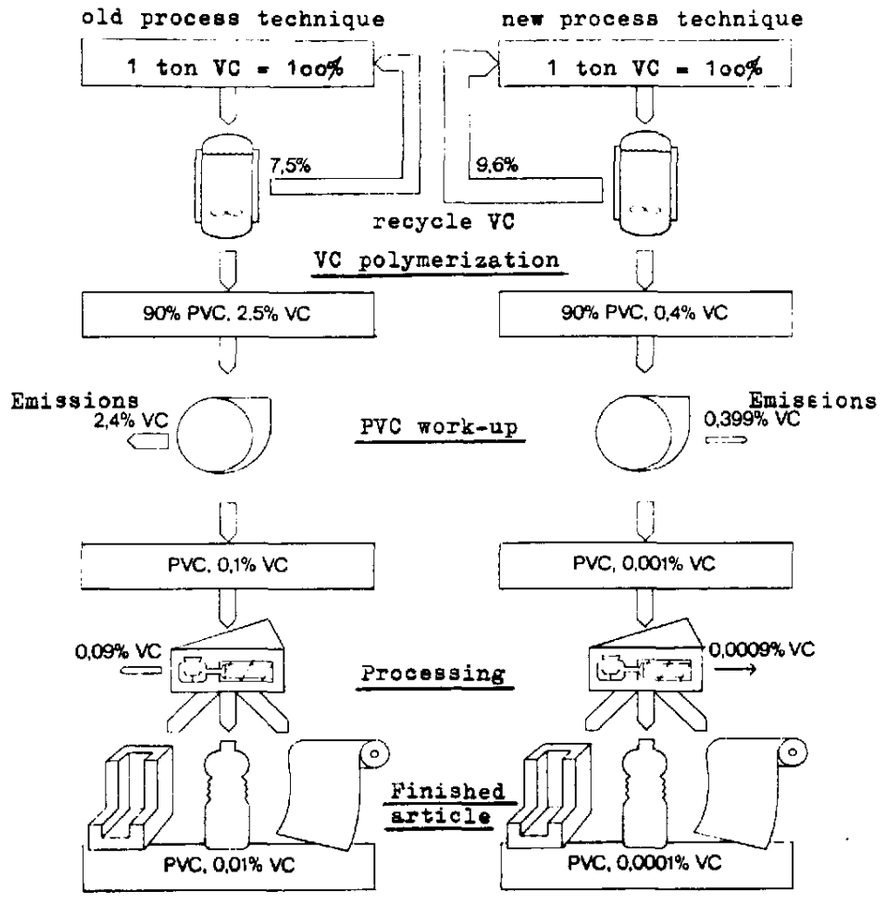
In consequence, the only conceivable solution to this set of problems is that the PVC leave the enclosed section of the production process with a considerably lower VC content than hitherto. To this end the development of suitable methods for intensive degassing has been spurred. The rough treatment this necessitated gave rise to considerable doubts as to the serviceableness of the PVC manufactured in this way, but the circumstances permitted no other alternative.

Contrary to expectation, the investigations instituted held out promise of success in finding a solution. The changes in the quality characteristics and properties of the PVC were so small that plants are already being converted to intensive degassing.

Depending on the prevailing production conditions, degassing can be carried out before or after the solids separation, but it has to be done before drying. It is important that open systems may be employed only after intensive degassing and that all prior stages must be enclosed and gas-tight.

The methods for intensive degassing have been developed by several PVC producers and made available in the form of know-how to all German PVC producers. It is remarkable that the development of this technology was possible in such a short time - practically within one year. First, laboratory methods of analysis for detecting minute quantities of VC had to be found. Then the instrument-making industry had to follow suit with automatic equipment for these analytical methods, as without automation the enormous number of VC tests on the polymer, the ambient air and the off-gas could never have been accomplished.

Effect of Intensive Degassing (example)



In the old process technique the polymerization of VC results in approximately 90% PVC and 7.5% non-reacted VC, which is pumped out and recycled to the production process. 2.5% VC is dissolved in the PVC, this corresponding approximately to the residual VC content. In the subsequent processing stages this VC residue is reduced by the emissions in case. In the new process technique it will be possible in future to achieve values in the finished product down to o.ooo1% VC, i.e. down to 1 ppm VC.

By applying this new process technique and the "ad hoc" measures, the industry has simultaneously succeeded in decisively reducing the residual VC content in the powder. PVC grades which formerly contained 500 - 1,000 ppm vinyl chloride today contain only 100 ppm VC or less. The residual VC content of several grades for various fields of application has even been reduced to 10 ppm and less.

It is the objective of the German PVC producers only to market PVC powder in future that has a VC content of not more than 10 ppm.

The methods of intensive degassing have as yet not fully matured and require to be optimized. But it is foreseeable at this stage already that this technology will be the basis for future PVC powder production. PVC will then fulfil purity requirements that are rarely demanded even in pharmaceutical specifications.

Health Protection in Processing

Simultaneously with the reduction of the residual VC content by the PVC producers to values below 100 ppm and for specific grades to below 10 ppm, the processing industry has in turn developed processes and measures of industrial safety to a stage where a risk to health for the workers can be ruled out, provided that the plant is efficiently managed and operated. Accumulations of VC in the work area are avoidable by instituting relatively simple measures. A technical guiding concentration of 5 ppm as the annual mean is aimed at here, too.

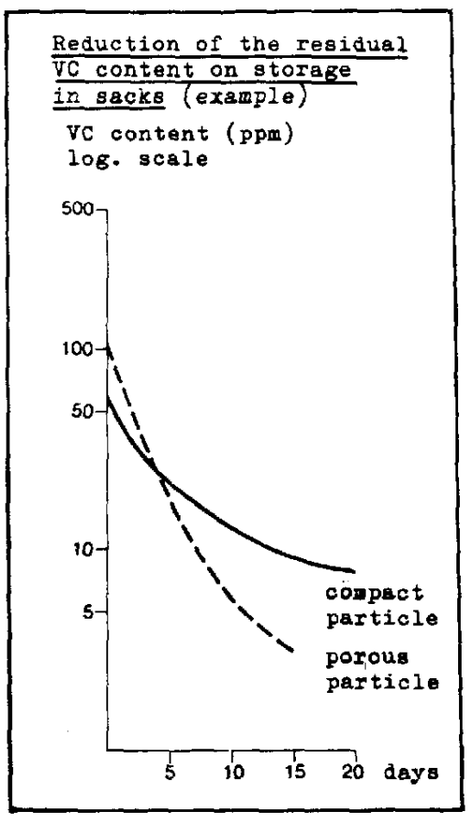
Storage

Since even at very low monomer contents in the PVC, measurable VC concentrations may occur due to degassing when the material is stored over prolonged periods in sacks, good natural or artificial ventilation must be provided.

No special measures are required for storage in silos; merely before entry for the purpose of cleaning and repairs should the silo be ventilated with ample fresh air and the VC concentration measured. If the material is not transferred in a closed system directly into the mixer, the silo discharge screw should be provided with a supply of fresh air.

Mixing

The residual VC content is reduced in the mixer to a fraction of its initial value by heating to 110 - 120° C. This has been confirmed by numerous measurements on many different


Reduction of the residual VC content on storage in sacks (example)
VC content (ppm)
log. scale
500
100
50
10
5
compact particle
porous particle
5
10
15
20
days

mixers. Further effective measures to reduce the VC content are the use of vacuum mixers or purging with air during the mixing process. However, it should be ensured that the exhaust air is discharged outside the building. This should be standard operating procedure in practice anyway.

Processing

Since, as in mixing, there are exhaust or ventilating devices at many points of the plant in moulding operations, no further measures are required. This applies also to the processing of semi-finished stock.

The concentrations of VC in the ambient air of PVC processing plants determined recently by the Berufsgenossenschaft der Chemischen Industrie(Professional Liability Insurance Association for the Chemical Industry) are in the region of 1 ppm. Injury to the health of workers in the PVC processing industry consequently ought to be ruled out in future.

The presumption occasionally voiced, viz. that depolymerization, i.e. re-conversion into monomeric VC might come about during PVC processing, particularly at elevated temperatures, has not been confirmed. All experiments in this direction, even under the most extreme conditions, have disproved this.

Protection of the Consumer

All endeavours towards reducing the VC concentration in the work area also serve to protect the consumer. The smaller the residual VC content in the raw material, the smaller the minimal, still measurable traces in finished articles.

Food Packings

The manifold protective functions which have to be fulfilled by packings of PVC for foods would be senseless if even the slightest risk were to arise for human beings.

Until two years ago only the high tightness to aroma, gas and moisture had been in view with respect to PVC packings, if oxygen-sensitive foods such as butter, margarine, oils, fats, mayonnaise, marinades and other preserved foods with limited keeping qualities were to be reliably protected from spoilage. Until that time it was still assumed that the gaseous, monomeric vinly chloride is degassed during

thermoplastic processing at the latest and that the finished mouldings are free of monomer. This opinion was reflected in the regulations of the health authorities of many countries. It was not until the further developed, considerably improved analytical methods were introduced that the picture was completely changed. They revealed that small residual traces of VC were in fact still contained in packings made of PVC and may partially migrate into the packed food, depending on the storage time, temperature and other conditions.

The test results known to date and the outcome of developments during the last two years, i.e. the drastic reduction of the VC content in all processing stages do not provide any reason why food packings of PVC should not be used. The values considered tolerable so far are several times higher than the low VC content achieved in PVC production and processing as a result of the measures taken, so that in all probability there is no danger to the health of human beings. Thus the expectation voiced at the 57th meeting of the Kunststoffkommission des Bundesgesundheitsamtes(Plastics Committee of the Federal Health Office) to the effect that manufacturer and processor alike should exploit all technical means to reduce the VC content, has been fulfilled.

A PVC packing, for example, which has been made from a powder containing 10 ppm residual VC still contains about 1 ppm VC. If one assumes that one-half of this PVC migrates outwards and one-half into the food, and if the weight of the packing is 100 g, the amount of food it contains is 1 litre = 1,000 g, then the residual amount of VC in the food is 50 ppb.[1]

Several countries have followed these technical possibilities in the meantime and have fixed limiting values of 50 ppb.

This figure corresponds to the analytical possibilities under the conditions of practice which have a true informative value only above 50 ppb.

Only the Food and Drug Administration (FDA) does not feel it can adopt this standard for the USA. In its latest proosal which comes into force in two months unless public hearings result in changes, the authority presumes a "non-detectability" of VC in food. The FDA proposes, furthermore, that unplasticized PVC packings should in future only be allowed in the USA under individual permits.

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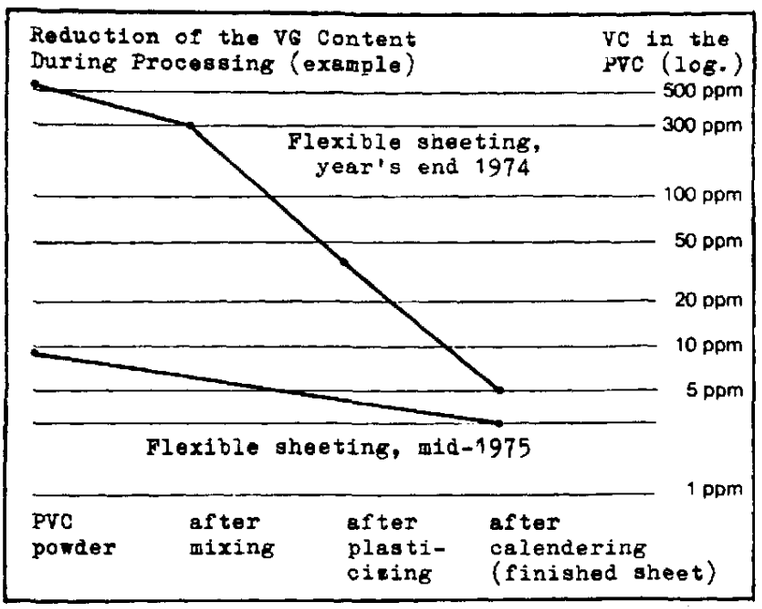
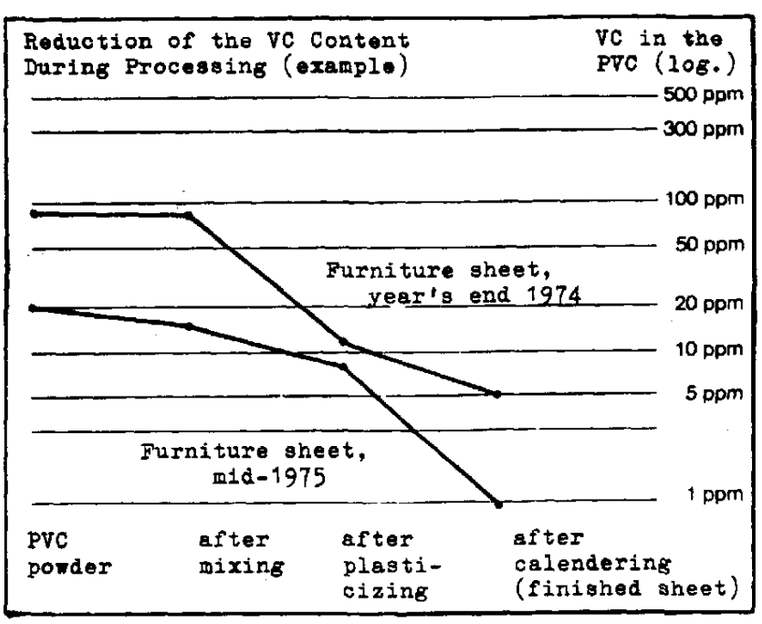
1) ppb = parts per billion


Reduction of the VC Content
During Processing (example)
VC in the
PVC (log.)
500 ppm
300 ppm
Flexible sheeting,
year's end 1974
100 ppm
50 ppm
20 ppm
10 ppm
5 ppm
Flexible sheeting, mid-1975
1 ppm
PVC
powder
after
mixing
after
plasti-
cizing
after
calendering
(finished sheet)


Reduction of the VC Content
During Processing (example)
VC in the
PVC (log.)
500 ppm
300 ppm
100 ppm
50 ppm
Furniture sheet,
year's end 1974
20 ppm
10 ppm
5 ppm
Furniture sheet,
mid-1975
1 ppm
PVC
powder
after
mixing
after
plasti-
cizing
after
calendering
(finished sheet)

This appraisal of the risk involved is not supported by the feeding tests conducted in animal experiment by Professor Maltoni in the Instituto di Oncologia. The outcome after a test period of one year was that of 80 experimental animals which had received 16.6 mg VC per kg body weight daily, one rat contracted an angiosarcoma. There were no findings in the feeding test with 3.3 mg.

The tests, moreover, currently being carried out at the Dutch Central Institut voor Voedingsonderzoek/TNO, commissioned by the German and Dutch PVC producers, have resulted in a "no effect dosage" in rats at 30 mg VC/kg body weight in a 90-day feeding test. Even 100 and 300 mg VC/kg body weight did not appear to constitute a "directly toxically acting concentration". The subsequent two-year test which has been running for 26 weeks has not revealed any indications of damage.

Other PVC Products

The physical characteristics of PVC extend from rigid/tough, for example in pipes, roller blind slats, gramophone records and window frame sections to soft/elastic in sheeting for shower curtains, sports articles, artificial leather, floorings, furniture sheeting, office film, cables and tubing. In view of the VC problem, complex criteria similar to those with respect to packing materials apply to these articles, too.

A transfer of vinyl chloride to humans by means of skin contact can be ruled out because of the short contact times and the low VC content in finished articles. The inhalation of traces of VC from these articles can only be calculated theoretically but is not detectable, even by means of the most sensitive measuring methods known.

Articles of plasticized PVC liberate vinyl chloride residues faster than unplasticized PVC, but owing to their processing and composition they contain smaller quantities of VC from the start. Consequently no health hazards arise on using and handling these articles. All calculations, even when taking into account the most unfavourable conditions, for example, in automotive interiors, floor coverings and building construction components, do not result in any values suggesting a danger to health.

Measuring Methods and Analytical Procedures

The control of VC residues in the respiratory air, in PVC powder, in the finished article and in food, requires sophisticated methods and highly sensitive measuring instruments, such as those developed recently. The methods formerly considered adequate, had to be improved to such an extent that continuous controls at extremely short intervals and under all conditions of practice can be carried out.

Measuring Ranges

The results of analyses are normally given in percentages. In gas analysis, percentages by volume are concerned whilst for solids and liquids the results are given in per cent by weight. In the case of very small values the concentrations are given in ppm or ppb.

It may be necessary in practice to convert into units of weight the volumetric data obtained by gas analysis. The following conversion factor is applicable:

$$1 \text{ volume-ppm VC} = 2.6 \text{ mg/Nm}^3 \text{ air.}$$

Limits of Detection

In trace analysis the limit of detection is a magnitude that can be stated only with difficulty. This applies in particular when on account of disturbing influences such as "blank values" or influences from the surroundings or the material under test, it is not possible to achieve the limit of detection that would otherwise be possible with the equipment available.

VC in the Atmosphere

Originally, VC concentrations in the air were only measured in order to prevent explosions, i.e. to be able to institute measures in good time so that acutely dangerous VC-air concentrations were avoided. Relatively crude measuring methods and occasional measurements are adequate for this purpose.

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1 ppm = 1 part per million = o.ooooo1 = o.ooo1% = $1o^{-4}$%

1 ppb = 1 part per billion = o.oooooooo1 = o.ooooo1% = $1o^{-7}$%

For VC control in the work area, automatic, unproblematical measuring systems are required which enable the concentrations at many different points in the building to be measured and recorded simultaneously. Only in this way is it possible to obtain an up-to-the-minute picture of the prevailing conditions in the different work areas. The reading of several measuring locations is done both by multi-channel switch systems and systems which aspirate the air in parallel.

In the control of the work areas the following main problems were encountered:

- extremely low VC concentrations in the air, but not distributed uniformly throughout the building
- frequent cross-sensitivity of existing measuring methods against other extraneous substances in the air
- regulations on explosion protection.

For the detection of leakages, moreover, fast-acting mobile instruments are required with the aid of which a VC concentration gradient can be investigated.

Although serviceable instruments have now become available for the various requirements, they cannot be universally employed. They have to be selected in accordance with the conditions prevailing in each case. Several tested and proven systems are therefore described in the following.

Test Tubes

For determining VC in the air, the method using test tubes and a hand pump is the simplest; however, it can only be used for single measurements. New developments have led to a limit of detection down to 0.5 ppm. The tube method is suitable for rapid single measurements on site, particularly because it can be carried out by untrained personnel. However, it is not adequate for continuous control of operations.

One disadvantage is that unsaturated chlorinated hydrocarbons are also included and the more sensitive tube types are desensitized by organic solvents.

FID Instruments

Instruments with a flame ionization detector (FID) are highly sensitive and operate continuously. They can be used both for stationary and portable measuring systems. Their measuring principle is based on the fact that ions are produced during the combustion of organic substances in a hydrogen-air mixture, which substantially increase the electrical conductivity. The amperage produced in each case is dependent upon the amount of organic carbon introduced. However, the instrument cannot distinguish between the individual hydrocarbons present in the air alongside VC. Although it is not selective, the instrument is quite useful, because the data provided are always on the safe side. The VC concentration can be lower, but never higher than indicated. The FID has the advantage of high sensitivity and a short response time (approx. 1 second). Consequently it is especially suitable for rapid, cyclic monitoring of several measuring locations, and also for leak detection.

Ionoflux Instruments

Ionoflux instruments also operate continuously, but their selectivity is greater. They measure the electrical conductivity of an absorption solution which increases proportionately to the VC content. The chlorine of the vinyl chloride (or other chlorinated hydrocarbons) is converted into hydrogen chloride in the process. The increase in conductivity corresponds precisely to the amount of VC introduced. The chemical reaction takes a certain time, consequently the measured VC concentration is recorded about three minutes after introducing the test substance.

Because of its increased timing constant the instrument is less suitable for monitoring and leak detection. In conjunction with parallel aspiration from several measuring locations in a room, however, it has the advantage of fully continuous registration of the true unit of time/space VC concentration means.

Gas Chromatographs

The highest degree of selectivity is achieved with gas chromatograph which, however, can only measure intermittently. It combines the advantage of selectivity with that of high accuracy and sensitivity. The flame ionization detector is coupled with a separating column which makes it possible to separate the sample according to boiling point, diffusivity or reactivity of its components. They successively enter the detector where they are determined quantitatively.

Determination of VC in the Air

Instrument	Limit of detection (ppm v/v)	Selectivity	Response lag	Disturbing factors
PID	o.2	low	1 sec	all hydrocarbons and ammonia
Gas chromatograph	o.2	good	1-3 min	none
Ionoflux	1.o	slightly restricted	3 min	halogenated hydrocarbons
Test tubes	o.5	restricted	1o-2o sec	unsaturated chlorinated hydrocarbons, organic solvents

Gas chromatographs are employed for stationary control, particularly where the use of a flame ionization detector would be senseless because of a high proportion of extraneous hydrocarbons. Both stationary and portable gas chromatographs are available. As an analysis with the instrument takes between one and three minutes, depending on the design, it is not suitable for leak detection.

Personal Dosimeters

For experimental purposes, personal dosimeters can also be used. They are small instruments carried on the person, continuously pumping air through a tube containing activated charcoal. The activated charcoal retains the VC which can be analysed in the laboratory later on. The mean VC concentration to which the person carrying the instrument was exposed can be deduced from the analysis. As such dosimeters are not explosion-proofed, they can only be used on an experimental basis in Germany. Further disadvantages are that evaluation is possible only subsequently (it is thus not a warning device), that only a mean for the period of measurement is obtained and that a tube can only be used for a limited time (between 1 and 4 hours).

Other Instruments

The ultrared absorption method was formerly used, too. In view of the present minimal concentrations and the limiting values that have to be controlled, it is no longer efficient enough. However, new developments of VC measuring instruments are to be expected in the future, as the industry is endeavouring to produce ever simpler and more sensitive instruments. Roughly on the basis of a kind of test paper.

VC in the PVC

The determination of VC with the FID following gas chromatographic separation is also the basis of the methods for analysing the VC content in the PVC. For this purpose the PVC, either in the form of powder, granules or the finished article, is dissolved in a suitable solvent, e.g. tetrahydrofuran or dimethylacetamide, and an analytical standard added for the quantitative determination of the VC content.

Two methods of working are available. One is based on the normal procedure in gas chromatography, in which the injected solvent including the VC and standard is vaporized directly and determined in the detector following separation in the column.

The other, more recent method, is based on the equilibrium between the above solution and the vapour phase which is formed in a closed vessel under defined conditions. The concentration of the VC in the vapour phase is then a direct measure of the VC concentration in the PVC under test. Out of the vapour phase of this vessel the sample is injected into the gas chromatograph and following separation, the VC is determined in the FID. This additional operation has resulted in the method being called the head-space method. It is employed both in manual and extensively automated operation; it has proved to be the fastest and most sensitive method, especially in series of analyses. The limit of detection of this method is approximately 0.5 ppm = 500 ppb VC in the PVC.

VC in a Simulation

In order to determine the migration of VC from the packing into foods the tests are carried out in so-called simulations. Usually 3 % acetic acid and 10 % ethanol are used as aqueous simulations for foods, whilst salad oil, for example, is used as a fatty simulation. The normal gas chromatographic methods for determining VC no longer meet the heightened demands of the extremely low limits of detection. For this reason the head-space technique must nearly always be employed for the VC determinations. The limits of detection achieved by this method go down to only a few ppb when using simulations, as opposed to the VC determination in the PVC. Here, too, the limits of detection can be considerably affected by blank values and disturbing influences of the environment. The limit of detection can frequently be improved by selecting suitable simulations with low blank values, and for carrying out reference measurements.

VC in the Food

Special difficulties are met with in the determination of very small VC concentrations in foods. Again the head-space method is the only practicable technique. The difficulties arise not so much from the analytical method, but rather from the unknown and frequently uncontrollable blank values by which the analytical result would have to be reduced in order to get at the true VC content. Analytical data for VC in foods consequently only have informative value above 50 ppb.

Sampling

A prerequisite for obtaining valid measured values is efficient sampling. It must be ensured that the sample constitutes a representative cross-section of the total. Common methods for obtaining such an average sample are mixing, quartering, dividing, grinding, etc. Where PVC in powder form is concerned, it must be considered that particles near the surface degas faster than those located in the centre. It is important, furthermore, that the sample is kept in a gas-tight container and is analysed as soon as possible.

Regulations in the Federal Republic of Germany

Betriebsverfassungsgesetz (Law on the Constitution of Enterprises)
Under the provisions of this law (Article 81) the employer is obligated, before employees start their jobs, to brief them on possible accident risks and health hazards, as well as the measures and equipment for preventing them.

Accident Prevention Regulations
Prior instruction and periodically recurring briefings for the prevention of accidents and hazards to health are also obligatory under the accident prevention regulations of the Professional Liability Insurance Association of the Chemical Industry.

Principles of the Professional Liability Insurance Association with respect to medical check-ups under the aspects of industrial hygiene.

The Professional Liability Insurance Association of the Chemical Industry, in collaboration with medical officers of industry, have introduced continuous medical check-ups of the employees, in addition to existing examinations. Before a job is started in certain sectors the suitability of the person concerned must be determined in a medical check-up; this has to be confirmed at regular intervals.

Technical Guiding Concentration

If the threshold limit value of a substance is suspended because of its carcinogenic properties, as was the case with VC, it may be replaced by a technical guiding concentration.

It is defined as follows:

"Observance of the technical guiding concentration in the work area is intended to reduce the risk of injury to health, but cannot completely exclude such risk. The technical guiding concentration is governed by the existing technical conditions and the possibilities of technical precautions, taking into account experience made in industrial hygiene in the handling of the dangerous working material. As the risk of an impairment of health is not fully excluded on observing the technical guidelines, endeavours must be made by means of constant improvements of the prevailing technical conditions and technical protective measures to obtain concentrations which are as far as possible below the technical guiding concentration".[1])

The Ausschuss für gefährliche Arbeitsstoffe (AgA) (Committee for Dangerous Working Materials) convoked by the Bundesminister für Arbeit und Sozialordnung (Federal Ministry for Labour and Social Affairs) in which experts of the Professional Liability Insurance Association, the Authorities and industry are represented, has fixed an annual mean of 5 ppm as the technical guiding concentration.

"For a period of one hour the concentration expressed as a mean value should not exceed the threefold technical guiding concentration. This technical guiding concentration applies particularly to

> the manufacture, recovery, storage, filling, conveyance and use of monomeric vinyl chloride,
> the conversion of vinyl chloride into non-fabricated vinyl chloride polymers (e.g. PVC production), the handling of non-fabricated vinyl chloride polymers and moulding compounds made from them.

For existing plants for the conversion of vinyl chloride into non-fabricated vinyl chloride polymers (e.g. PVC production) a technical guiding concentration of 10 ppm is fixed. As transitory regulation for these plants a value of 20 ppm will be permitted until 1st July 1976.

The technical guiding values will be revised by 1st January 1977 and adapted to the state of technical development, utilizing the latest experience in industrial hygiene".[2])

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1) "Arbeitsschutz" No. 5/1974, p. 170

2) Notice of the Bundesminister für Arbeit und Sozialordnung of 19th March 1975-III b 4-3880.7- 1357/75, published in "Arbeitsschutz" No. 4/1975, p. 127

Guidelines regarding protective measures for the prevention of injury to health when handling vinyl chloride.

These guidelines are intended to ensure that the employee is exposed to the lowest possible VC concentration in the work area through continuous improvements to the technical conditions. The technical guiding concentration in force at a given time serves as the value of orientation since it is a concentration that is checked in accordance with the current state of the knowledge in industrial hygiene and is adapted to the technical development, as well as the analytical possibilities.

According to the aforementioned guidelines the respiratory air in the work area has to be continuously controlled by carrying out measurements of the VC concentration. They also include regulations on adequate measures of ventilation and personal protection - especially respirators - for work in the course of which contact with VC must be expected.

Threshold Limit Value for PVC Dust

The maximum permissible PVC dust concentration for inert dusts in work areas, e.g. in bagging stations, is limited to 8 mg/m^3 by a threshold limit value regulation of the Deutsche Forschungsgesellschaft (German Research Association). PVC powder, i.e. dust is classified as inert.

Law on the Traffic with Foods, Tobacco Products, Cosmetics and other Commodities

In Article 31, the Lebensmittel- und Bedarfsgegenständegesetz (Food and Commodities Act) prohibits the use of articles from which substances migrate into foods, expect amounts unobjectionable from the aspect of health, odour and taste which are unavoidable on technical grounds.

In order to ensure that the composition of plastics is unobjectionable from the health aspect, the "Kunststoffkommission des Bundesgesundheitsamtes" (Plastics Commission of the Federal Health Office) was convoked in 1957.

The Commission draws up positive lists with respect to the individual types of plastics (PVC, polyethylene, etc.) which show the individual starting materials, auxiliaries and additives, partly with the quantitative limits and their analytical detection. These lists are published in the Bundesgesundheitsblatt (Federal Health Gazette) and recommended as the basis for assessing plastics.

The Plastics Commission has dealt with the question of VC monomer on several occasions.

Bundes-Immissionsschutz-Gesetz (Federal Clean Air Act)

In order to minimize influences detrimental to the environment, all plants concerned are subject to approval under the Federal Clean Air Act of 15th March 1974 or have to meet the requirements of subsequent regulations (Article 17).

The basis for this is the TA-Luft (Technical Regulation for the Prevention of Atmospheric Pollution[1]), an administrative directive for the Gewerbeaufsicht (Industrial Inspectorate). Accordingly, a permissible emission concentration of not more than 150 mg/Nm^3 exhaust air applies to VC, insofar as 3 kg VC/h is exceeded.

In off-gas volumes of more than 70.000 m^3/h the mass concentration of the total dust must not exceed 150 mg/m^3 off-gas. The mass concentration of the dust contained in the total dust with a particle size smaller than 10 µ may at most be 100 mg/m^3. Other limiting values which are laid down in the TA-Luft apply to smaller off-gas volumes.

Limitation of the Ambient Air Concentration for VC

In addition, extraordinarily low limiting values for ambient air concentrations have been laid down exclusively for North-Rhine Westphalia. Here, at a cumulative frequency of 99 %.

UBA 10009

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1) Gemeinsames Ministerialblatt, vol. 25, No. 24/1974, 17th edition, p. 425