GERMAN Literature on VC/PVC: MEASURES FOR HEALTH PROTECTION

2/24/75

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SPI

THE SOCIETY OF THE PLASTICS INDUSTRY, INC.

250 PARK AVENUE · NEW YORK, NEW YORK 10017 · 212/573-9400

January 17, 1975

TO: Members of the VCM/PVC Producers Group

SUBJECT: German Literature on
VC/PVC: MEASURES FOR HEALTH PROTECTION

Attached is a copy of a translation made available through the courtesy of Air Products and Chemicals, Inc. This is the literature that Dr. Ross Adams discussed at the December 6th meeting of the VCM/PVC Producers Group. It appears to give an up to date status on the German knowledge of this problem.

Respectfully,

John R. Lawrence

John R. Lawrence
Director of Technical Liaison

JRL:jo
Attachment

VC/PVC: MEASURES FOR HEALTH PROTECTION

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Vinyl Chloride (VC) is feedstock for one of the most frequently used and most versatile plastic materials, Polyvinyl Chloride (PVC).

Recent scientific findings lead to the suspicion, that VC gas in certain concentrations has a carcinogenic effect.

Knowledge and suspicions which in this connection have been accumulated over approximately 1 year are news to science as well as regulatory authorities and the industry worldwide.

This pamphlet attempts to explain the present state of knowledge and findings. In addition we would like to point out directions for safety measures which have to be followed in the plastics industry.

It is possible that new evidences have been accumulated since this pamphlet has gone to printing.

Waiting for these, however, is not feasible. We are primarily concerned to convey the understanding of this problem not only to the PVC processing industry but to larger areas of the public.

Dated:

Frankfurt/November 12, 1974

PVC-PRODUCTION

PVC has been manufactured in the Federal Republic for over 30 years.

Consumption

Production for 1973 was 1,034,000 metric tons with a value of approximately 1 Billion(German marks)DM. PVC is used in almost all areas of the economy whereby primary industries such as the construction business, electrical industry and the automotive industry are particularly heavily dependent on this plastic material.

PVC-Consumption 1973	%
Pipe and Fittings	23
Flooring	10
Cable Installations	11
Films (Flexible and Rigid)	22
Profiles, Including Windows	9
Coated Fabrics (Artificial Leather)	4
Venetian Blinds, Building Tiles, Fascia	6
Bottles	2
Ribbons, Strings, Ropes	2
Hose	2
Records, Shoes, Driving Belts, Conveyor Belts, Foam Materials	9
Total	100

Polymerization of VC

PVC is commercially manufactured in the Federal Republic by three different methods:

Emulsions-Polymerization

Suspensions-Polymerization

Bulk-Polymerization

Polymerization of Vinyl Chloride to Polyvinyl Chloride is conducted at temperatures between 40° and 80°C at a VC vapor pressure of approximately 6 to 14 atmospheres. At atmospheric pressure, Vinyl Chloride has a boiling point of minus 13°C and during polymerization, is dissolved in significant amounts in the produced PVC. These dissolved quantities are converted into PVC to a large degree, as the polymerization process progresses.

The speed of any chemical reaction depends on the concentration of the used raw materials. Consequently polymerization of VC to PVC is slowed toward the end of the reaction since the concentration of the monomeric VC in the reaction mixture is constantly decreased. Theoretically it would take forever to await polymerization of the residual VC. Hence the reaction is stopped depending on the process used, after approximately 90% of the VC has been polymerized. The point in time at which the reaction is stopped is essential for the properties which are desired and necessary for further processing. In all processes termination is achieved by evacuation of the residual VC gas from the autoclave. It is recovered by liquifaction and is recycled to the production process.

Economic reasons dictate a recovery as complete as possible since it is substantially more difficult to recover VC gas which escapes during further processing steps such as drying, classifying and movement within the plant. In spite of a massive amount of technical efforts, the removal of VC gas as present in small amounts in PVC particles has been unsuccessful to date. This is difficult to comprehend in recognition of the fact that Vinyl Chloride boils at minus 13°C and is temporarily exposed to temperatures up to 250°C during the drying process. The reason for this is (understood to be) ↓ as follows:

The liberation of monomer which is dissolved in PVC occurs on the surface of the individual PVC particle, on to which it diffuses (migrates) ↓ from the inside. This diffusion process is defined by the drop in concentration toward the surface, the length of the diffusion path and above all by the temperature.

WORK RELATED MEDICAL PROBLEMS

A narcotic effect upon inhalation of VC had been recognized (as early as the 1930's when the) ↓ large scale use of VC had reached significant proportions.

Not until the beginning of the 1960's did scientists discover diseases such as acroosteolysis, scleroderma and liver diseases.

Maximum Concentration At the Place of Work

A committee of the German Research Association (DFG) specifies maximum exposure levels (MAK) for purposes of health protection in production operations for VC as well as for many other chemicals.

In 1966 a MAK value of 500 ppm had been specified in Germany. The committee for testing of hazardous materials of the German Research Association defines the MAK value as the concentration of a gas, vapor or particle suspended in air at the place of work, which,based on present knowledge,does not impair the health of the worker under repetitive and long lasting exposure usually 8 hours per day, however, not to exceed 45 hours per average work week.

Studies by the American professor T. R. Torkelson [1], led to the reduction of the MAK value to 100 ppm after he discovered histopathological liver alterations in his animal tests with rats exposed to 200 ppm during a period of 6 months.

Yet the reference book "Chemistry and Toxicology of Plastic Materials" explained as late as 1970: "Vinyl Chloride is a gas with relatively low toxicity. In higher concentrations it has a slightly anesthetic effect and causes irritation of the eyes."

First Indications of Cancer Threat

Investigations known until then had not produced any evidence of a possible cancer threat by Vinyl Chloride. The connection between Vinyl Chloride and a cancer threat as recently treated in frequent discussions, has been documented in studies by Professor Viola [2] for the first time in 1970. His tests with rats however, were conducted at unrealistically high doses, which up to 30,000 ppm bordered on the explosion limit of a VC/air mixture.

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1) American Industrial Hygiene Association, Journal Volume 22, Page 354

2) Presentation, 10th International Cancer Congress, 22-29 of May 1970, Houston, Texas

Professor Maltoni of the Oncological Institute, Bologna, Italy was commissioned an international group of companies to explore in depth the effects of VC under actual operating conditions. Preliminary reports issued in the summer of 1974 show that rats which had been exposed up to 1 year to a range of VC concentrations from more than 200 to as low as 50 ppm, have contracted angiosarcoma of the liver, a special cancer of the liver.

In the U.S. Bio-Test Laboratories in North Brook, Illinois detected almost simultaneously the same liver damages in mice after 7 months exposure to 50 ppm VC. As an emergency measure the use of VC as propellant in aersol sprays was prohibited in the United States and stopped in West Germany.

Cases of Illness in West Germany

Professor G. Veltman of the University Clinic for Skin Diseases, Bonn, West Germany had previously determined the danger of VC to the human body on workers which had been employed in PVC production. As a result in recognition of important discoveries in the area of industrial medicine and worker protection, he and his co-workers received the Franz Koelsch Reward donated by the Manufacturers Association of the Chemical Industry.

Through the end of August 1974 a total of 124 suspected cases of the "so-called VC disease" had been reported by a few PVC producers in the Federal Republic. Social Security insurance carriers have recognized 43 of these cases as occupational diseases.

The medical definition of these 43 recognized cases are primarily specified as Raynaud's Syndrome, liver and spleen damages, thrombocytolysis and reticulocytosis.

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41 of the afflicted persons have in the meantime resumed employment. Professor Veltman's studies revealed that,in the severe cases a change had been diagnosed in lung, liver, spleen, skin and vascular systems. His,as well as simultaneously publicized studies in other countries gave the signal for a retroactive investigation of the causes for the death of workers previously employed in VC and PVC production. Three cases of hemangioendotheliosarcoma of the liver, a very rare case of cancer, have been diagnosed in this connection in the Federal Republic:

A worker,who died at the age of 38 and who was employed from 1956 through 1968 e.g. 12 years in a PVC production plant, last as polymerizer scrubber.

A chemical worker who had been employed for 11 years in a PVC producing plant and who died at the age of 39.

An operator who was employed in the filling of aerosol spray cans in which VC had been added as a propellant. He had been exposed to VC a minimum of 14 years and died at the age of 43. A liver fibrosis with enlargement of the spleen and esophageal varicosis had been diagnosed during his lifetime.

Studies to determine the extent of correlation between these deaths and VC in these plants are still under investigation.

Hence it is too early to finalize a conclusion on the extent of the existence of this disease. The examination of the causes for death are rendered more difficult as a post diagnosis does not lead to reliable results, and as to date angiosarcoma has been found only after more then 10 years exposure.

Research Studies

In addition, to date there is no unequivocal proof that the occurred symptoms of disease can be attributed exclusively to the influence of VC. In view of this the Ministry for Work and Social Order has commissioned a research project to clarify if process related impurities in VC could be considered as cause for the disease.

Further research projects for the elucidation of the VC disease are being conducted in cooperation between the Professional Trade Organization of the Chemical Industry, the Federal Ministry for Work and Social Order and the State Government of Nordrhein-Westfalen. Participants are: Professor Dr. Henschler, Institute for Toxicology and Pharmacology, University of Wurzburg, Professor Dr. Lehnert, Central Institute for Industrial Medicine, University Hamburg, and the State Physician for Industry of Nordrhein-Westfalen, Dr. Reinl, Dusseldorf. In particular these studies include the effects of VC on the human organism (investigations of metabolism), the compilation of a literature survey and evaluations as well as epidemiological investigations (determination of illness risk factors by differentiated group comparison). The Central Institute for Food Research in Zelst, Holland was commissioned by the Society of the Plastics Industry and PVC producers in Holland to conduct a 90 day feed test to determine the oral toxicity of VC in rats with ratios of 0, 30, 100 and 300 mg VCper kilogram body weight. At a ratio of 30 mg VC per kilogram body weight, these studies resulted in a "dosage without effects". 100 and 300 mg VC per kilogram did not result in "concentrations with direct toxic effects." Further information is expected as a result of a follow-up 2 year test for the determination of objectionable VC concentrations.

Emergency Measures

After recognition of these problems it would have been irresponsible to await results from further long term studies. Emergency measures for the reduction of risk at the place of work in PVC producing plants where hence applied as deemed necessary. This is reported in Document 7/1627 of the House of Representatives by the State Secretary of the Ministry for Work and Social Order on January 29, 1974 in response to an inquiry by a State Representative. Guidelines for safety measures to prevent injuries due to handling a Vinyl Chloride were significantly tighten in April 1974 in cooperation between the Trade Union of the Chemical Industry and specialists (from) the plastics producing industry. Additionally, continuous observations of employees were introduced in cooperation between Trade Union and experts (from) the industry in industrial medicine over and above the ongoing preventive medical examinations. They are documented in the July 1974 issue of "Principles for Preventive Industrial Medical Examinations" by the Trade Union.

Suspension of the MAK Value

A reduction of the established MAK values has been investigated in connection with the introduction of a variety of measures. In this connection the Commission for the Investigation of Health Hazardous Materials had to consider, that the handling of potentially carcinogenic materials require special safety measures and precautions in health protection. Such materials have therefore for some time been eliminated from the (published) list of MAK values and have been reported separately. VC has been added to the list of carcinogenic materials in view of the results from (the) animal experiments and the experienced

cases of illness. The previously established MAK value was suspended.

The Commission for the Investigation of Health Hazardous Materials issued a related statement dated June 14, 1974:

"The handling of proven or (potentially) carcinogenic materials requires special precautions and measures for health protection. Hence these are specifically enumerated and classified as those which

a) can cause severe tumors as experienced in human beings

b) so far have only been investigated by animal tests under conditions, which are comparable to possible exposure of human beings in the work process and which in the opinion of the Commission have definitely proven to be carcinogenic:

- e.g. Vinyl Chloride

Vinyl Chloride (containing) only (amounts of) minor impurities (was) definitely carcinogenic by animal tests. A special type of liver tumor (hemangioendotheliosarcoma) has been observed with workers which had been exposed to high Vinyl Chloride concentrations in specific work locations in the PVC producing industry. A causal correlation is imminent, at this stage, however, not (yet) proven. It remains to be seen whether the recently introduced in depth toxicological investigations as well as the retrospective stipulations with regards to employees' contact with Vinyl Chloride confirm or invalidate this relationship."

Technical Standard Concentration for VC

A so called "Technical Standard Concentration (TRK)," akin to that established for benzene, is to be established following the suspension of the MAK value by a Committee for Dangerous Materials (AgA) organized by the Ministry for Work and Social Order which is composed of representative experts from trade union and industry. This standard is defined as follows:

"Compliance with the Technical Standard Concentration at the place of work should reduce the risk of a health hazard, is however unable to completely eliminate this risk. The Technical Standard Concentration is based on technical circumstances and possibilities of the technical prophylaxis (in conjunction with) work related medical experiences in handling dangerous materials. Compliance with the Technical Standard Concentration does not completely eliminate the risk of impairment of health; hence by continuing improvements of the technical circumstances and the technical measures (for protection,) concentrations have to be aspired which fall as far below the Technical Standard Concentration as possible." [1)]

Up until the suspension of the MAK value for VC, according to a release by the Federal Ministry for Work and Social Order of May 22, 1974, a 50 ppm level was (adopted) as recommended by the Trade Union of the Chemical Industy. The soon to be released Technical Standard Concentration is expected to be lower. The continuous analytical monitoring of such low VC concentrations in the work (place atmosphere) is expensive. Hence it is imperative that producers and (processors) of PVC familiarize themselves (with,) and work toward integration of the expected parameters.

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1) Work Protection Issue #5/1974, Page 170

A program of regular medical examinations of the employees is already self-evident. The work safety law requires these for all industrial areas starting January 1, 1975.

RESIDUAL VC IN PVC

Polymerized PVC contains a residual amount of VC based on production related technical parameters as explained above. Depending on its viscosity, particle size and particle size distribution, as well as ambient temperature this residual VC migrates to varying degrees to the ambient atmosphere.

An exponentially declining curve results if the residual VC contents are plotted over time. This curve has a steeper slope with porous than with dense products and its slope increases also with increasing temperatures. The possibility for the lowering of the residual amount of VC in PVC are defined by-time,

- path of diffusion,
- temperature.

Time Relationship

The hereto customary allowance for gas diffusion would have to be extended significantly - to days or even weeks - in order to achieve a significant reduction in the residual VC content. An extended residence time in dryers or degassing equipment under presently used temperature conditions would damage PVC by thermal degradation not to mention the warehousing problems which would be caused by such measures. A temperature reduction during degassing on the other hand would mean a further prolongation of the process. Specially equipped degassing installations would have to be constructed during. Adopting appropriate measures compounding seems a more reasonable approach today.

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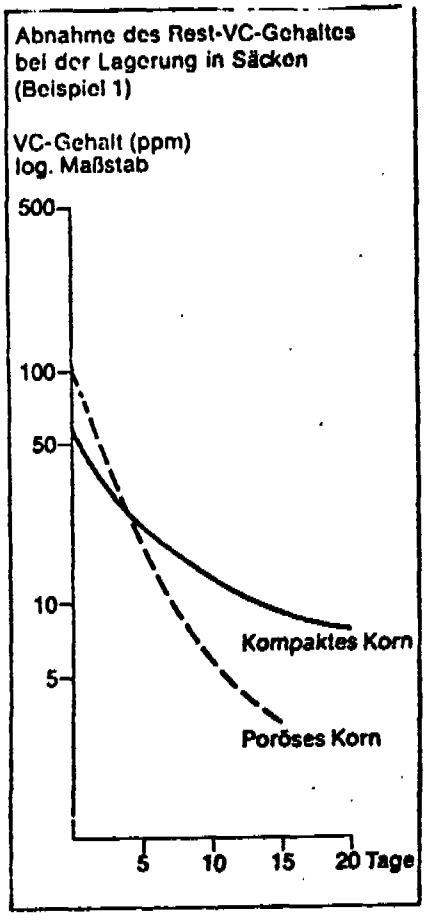


VC-Content (ppm)
log. scale

Dense Particle

Porous Particle

Days

Abatement of Residual VC in PVC During Storage in Bags

The two curves show the development for two types of PVC with approximate (viscosities) equal ↓ whereby the curve with the flat slope represents a relatively dense particle (while) ↓ the other curve represents a porous particle.

Path of Diffusion

The length of the path of diffusion during degassing depends on

- the particle size, the larger the particle the longer the path of diffusion.

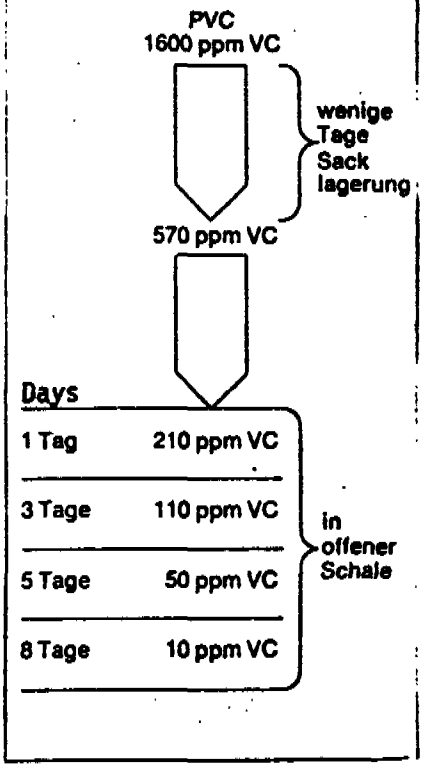
- the particle density, e.g. porosity and porosity characteristic. The more pronounced the porosity or specific surface area, the shorter is the diffusion path.

Production of a variety of end-products and the application of specific processing techniques would be impossible if PVC were exclusively produced to obtain optimum particle properties for degassing purposes. The market requires PVC properties ranging from the finest to the coarsest and from the most porous to the gel particle. The viscosity of PVC a function of polymerization temperature also influences its porosity. The higher the polymerization temperature, the lower the viscosity and the denser the particle.

Temperature Relationship

Degassing of PVC is accelerated with increasing temperature. Limiting, however, is the thermal stability of PVC. The addition of stabilizers at this stage is hardly suitable since the scope of application for the product would be significantly reduced. Hence commercial PVC contains a certain amount of residual VC. It follows that preventive measures have to be taken in the area of processing as well in order to prevent a health hazard by VC volatility.

Abnahme des VC-Gehalts in Abhängigkeit von der Lagerzeit (Beispiel 2)

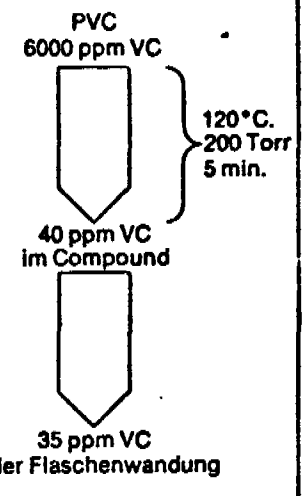


Reduction of VC-Content as a result of warehousing time

Warehousing for several days in bags

In open cup

Modellversuch mit einem PVC-Muster von extrem hohem VC-Gehalt.
Bei hoher Temperatur und Vakuum sinkt der VC-Gehalt in wenigen Minuten auf Bruchteile des ursprünglichen Wertes ab
(Beispiel 3)



Small scale test on PVC with extremely high VC-Content

Under high temperatures and vacuum, VC-Content drops in a few minutes to a fraction of the original level

200 mm Hg.

in compound

in blown bottle wall

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HEALTH PROTECTION IN PROCESSING AREAS

We therefore present here some ideas on how to avoid accumulation of VC in the work area atmosphere.

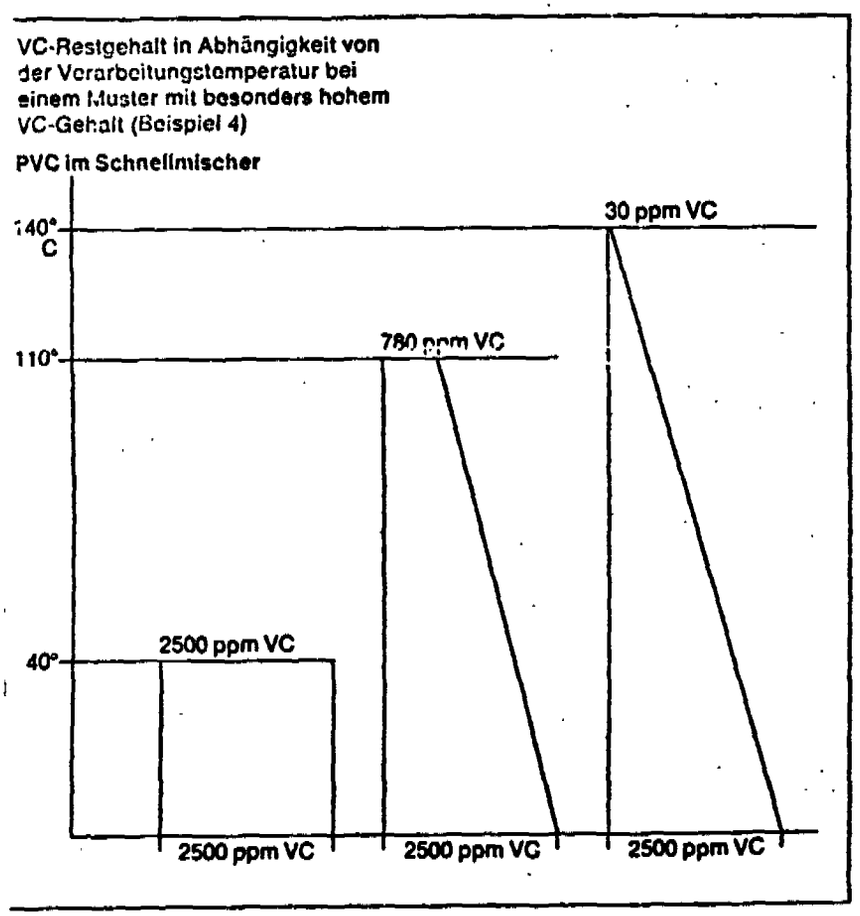
Storing

No special precautions are necessary for storing in silos, with the exception of access during maintenance and cleaning operations. Ample ventilation on the other hand should be provided in storage areas for bagged material in order to prevent accumulation of excessive ↓ VC concentrations.

Mixing

Most processing methods which do not require pellets or ready made compounds are preceded by mixing operations. Intensive mixers ↓ as used today and particularly the application of higher temperatures, stimulate and accelerate the liberation of residual VC from PVC thereby eliminating the major portion of the monomer. On one hand this presents an advantage as PVC processed in such a manner contains but traces of VC. On the other hand, however, it necessitates safety measures for mixing areas and equipment.

Up to several hundred ppm VC have been detected at mixer openings. Under any circumstance ↓ this is significantly higher than the pending standard levels. It is therefore imperative that these mixers are not vented toward the general plant area. The processing sequence of silo, mixer, cooler, processing equipment should for the same reason operate as a closed system with ventilation toward the outside. VC concentration in the mixing area can be held under 10 ppm by these measures.



Residual VC contents in relation to processing temperatures on a sample with particularly high VC content. PVC in the intensive mixer.

In general terms hot mixing entails advantages, since significantly larger proportions of VC are driven off than during cold mixing as shown in the following examples. This ensures that none or only very small amounts of VC are released in further processing steps.

Extruding

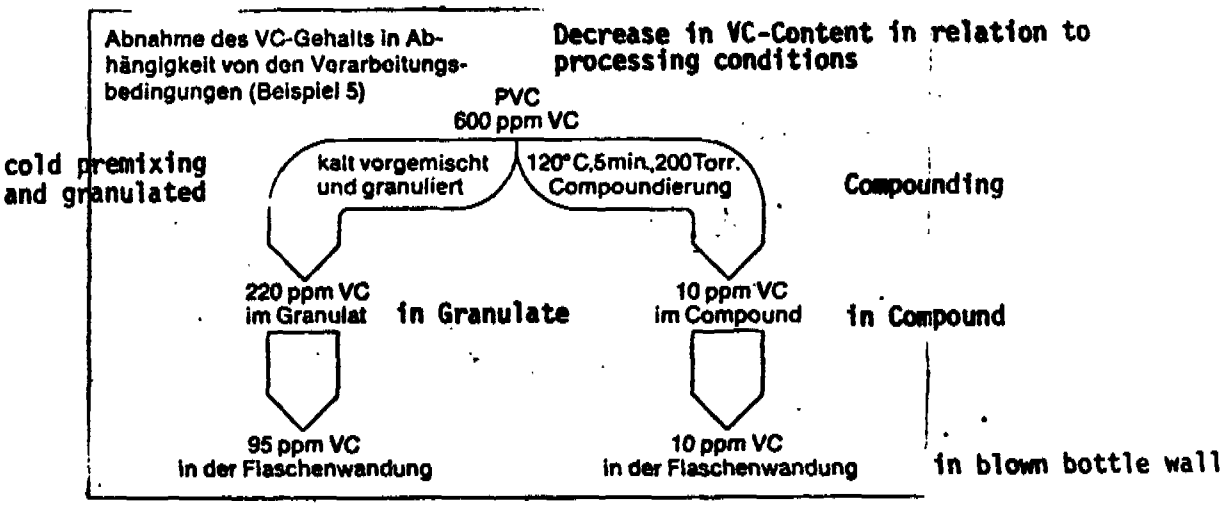
A variety of tests confirmed that the evaporation of VC from PVC is significantly impaired after thermoplastic conversion into finished products. This also applies to the hot melt as it emerges from processing equipment. Indicative is the measurement of a 10 ppm VC level obtained directly at the exit of a large scale granulator. Special precautions have to be taken at the hopper when processing powder blends, as heating accelerates the VC degasification. The recommendation goes to provide for sufficient ventilation at this point or even better to operate an enclosed system.

Injection Molding

Monitoring the VC concentration in the vicinity of injection molding machines both in the Federal Republic as well as in Great Britain showed also a level under 10 ppm. Recommendations made for extrusion processing apply here as well.

Calendering

In the calendering process attention should be concentrated on the initial processing steps. Mixing as well as preplastification equipment have to be equipped with sufficient ventilation. Work areas around


Abnahme des VC-Gehalts in Abhängigkeit von den Verarbeitungsbedingungen (Beispiel 5)
Decrease in VC-Content in relation to processing conditions
PVC
600 ppm VC
cold premixing and granulated
kalt vorgemischt und granuliert
120°C,5min.,200Torr. Compoundierung
Compounding
220 ppm VC im Granulat
in Granulate
10 ppm VC im Compound
in Compound
95 ppm VC in der Flaschenwandung
10 ppm VC in der Flaschenwandung
in blown bottle wall

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processing equipment are relatively free of VC exposure as calenders are already equipped with adequate (ventilation) ↓ units for the elimination of plasticizer and additive fumes.

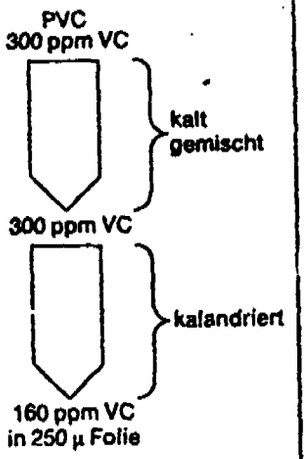
Paste Processing

Only minute traces of VC are liberated during processing of paste formulations from emulsion PVC at room temperature. This is primarily attributable to the fact that emulsion PVC has the lowest residual VC content of all three types of PVC. Typically, installed (ventilation) ↓ apparatuses which serve to eliminate plasticizer fumes during the curing step are satisfactory to eliminate traces of VC as well. Mandatory incineration equipment, which is required for the elimination of organic vapors at these large scale processing installations, provides an additional safety measure.

VC CONTENT IN THE FINISHED PRODUCT

Up until two years ago it was generally accepted that monomeric Vinyl Chloride gas would have evaporated completely by the time it reached the thermoplastic processing step and that consequently finished parts were free of monomer. This perception provided the basis for regulations as established by health authorities in many countries. Similarly in the U.S.A. PVC was classified in a group of materials generally considered as nontoxic with the designation of "prior sanctioned material."

Beim Kaltmischen bleibt der VC-Gehalt unverändert. Anschließendes Kalandrieren ist hinsichtlich der VC-Reduzierung nicht sehr effektiv (Beispiel 6)



VC-Content remains unchanged by cold mixing. Subsequent calendering is not very effective in the reduction of VC.

Cold Mixing

Calendered

in 0.25 mm Film

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In the spring of 1974 reports from the U.S.A. indicated that a 20 ppm VC content had been found in whiskey which was contained in PVC bottles. Subsequently the Food and Drug Administration prohibited the packaging of alcoholic beverages in PVC bottles. In spite of concentrated efforts (to date), no further information could be obtained with regards to the PVC or the analytical methods (used in this instance in the U.S.A.). The following investigations were conducted in Germany in order to clarify the circumstances:

Development of more accurate and improvement of known analytical methods.

Investigation of VC migration into food products from consumer products such as packaging materials.

Investigation of the impact of processing characteristics on the VC concentration in consumer product

Representative food products and storing conditions such as stipulated in the recommendations for consumer products by the Federal Health Administration were used for the investigation of the migration of VC from PVC packaging materials. The following representative food products were used: water, 30% concentration of acetic acid, 10% concentration of alcohol and edible oil. They were stored in PVC bottles for 10 days at 40°C, which at room temperature corresponds to a time period of several months. 40% and 50% alcohol concentrations were included in order to verify the surprising results as reported in the U.S.A.

The applied analytical methods (had) a minimum detection level of 0.2 ppm with the solutions in water and 1 ppm with edible oil.

Test results were generally below or in the vicinity of the minimum detection level even with relatively high VC concentrations in the bottle wall and hence fell significantly below the 20 ppm VC (as) detected in the U.S.A.

The Commission for Plastic Materials of the Federal Health Administration comments on the "examination of consumer products (produced) from PVC according to the latest state of scientific knowledge":

"The Commission for Plastic Materials of the Federal Health Administration reports in its 57th Session, that to date there are no indications of a health hazard by consumption of food products which had been packaged in PVC. Experimental 90 day animal tests had been concluded in September 1974 by the Dutch Central Institute for Food Research during which substantially higher amounts of VC had been administered (than those) which could possibly be expected as a result of contact of PVC with food products. There were no indications of a toxic effect. In view of this the oral intake of traces of VC with food products has to be treated in a different way then the intake of VC by inhalation.

Analytical tests on a broad range of food products which were packaged in commercial PVC resulted exclusively in levels below 1 ppm VC (e.g. less than 1 mg (VC per kg. of) food product). These tests are presently continued on a broader scope. Based on animal testing and analytical results the Commission for Plastic Materials of the Federal Health Administration has no reservations if (as a precautionary measure) the VC content in food products is limited to 1 ppm until new evidence is presented as a result of the commissioned long range tests.

The Federal Health Administration expects that all technological possibilities for a reduction of the VC content in the production of PVC materials as well as in its conversion to consumer products will be adopted."

The Food and Drug Administration in the U.S.A. to date has considered a limitation of the VC content to 10 ppm in finished products which are destined for contact with food products; according to the latest information, however, it is expected that the FDA is working toward an arrangement with which the industry is presently able to comply. The FDA has not arrived at a decision yet whether to impose a VC limitation in the finished product or in food products or respectively in representative test media and what the level of such limitations should be.

METHODS FOR MEASUREMENT OF VC

Refined methods have to be applied and highly sensitive instruments have to be used for the control of VC concentrations in the ppm range. This applies to monitoring of work place conditions in PVC producing and processing plants as well as to securing the consumer protection in PVC packaging of food products and to the determination of the residual monomer in PVC.

Drager Capillary

Until now the detection level of the most simple and economical method for the determination of VC in air has sufficed: the analysis by the "Drager Capillary Vinyl Chloride 100/a," in which air is being sucked through the capillary with a hand pump. If after 40 strokes the color of the capillary is unchanged, then the VC level in the air lies below 50 ppm. It can hardly

be expected, however, that this detection limit will suffice for plant monitoring purposes. The Drager Capillary will, however, retain its significance in a quick spot analysis, particularly since it has a relatively high reliability. Reaction with Potassium Permanganate (which serves as indicator) occurs aside from Vinyl Chloride only with a limited number of other mostly unsaturated organic compounds such as ethylene or chloroprene. These should however only (be present) rarely in conjunction with VC.

FID-Method

A significantly more sensitive method, which dependent on instrument design can be applied (for) spot or constant monitoring in exhaust ducts, capitalizes on the fact that during incineration of organic substances in a hydrogen-air- (mixture,) ions are created which significantly increase the electrical conductivity. Inside such a FID (instrument) (flame ionization detector) the flame burns (within) an electrical field which is created between the torch nozzle and a (counter) electrode by the application of approximately 200 volts. The resulting ions move in this field, - the resulting amperage is approximately proportional to the amount of the introduced organically bound carbon. The detection level of the FID could (conceivably) be lower than 1 ppm, if its selectivity would permit this. It responds practically to all organic compounds, such that (only known) conditions in existence at the test location would allow a judgement as to what substance caused the signal. At low concentrations this naturally is always an uncertainty. Advantageous is its fast response of approximately 1 second which allows rapid and successive monitoring of several locations.

Ionoflux-Instrument

Ionoflux instruments work also on a continuous basis, however with higher selectivity. Here the increase in electrical conductivity of an absorption solution, which is proportionate to the VC content, is being measured. Initially the VC is burned with a catalyst whereby hydrogen chloride and chlorine are derived from chemically bound chlorine. Subsequently both gases are absorbed in a hydroxylamine solution, whereby the chlorine is converted to hydrogen chloride. The increasing conductivity caused by the total amount of hydrogen chloride corresponds exactly to the introduced amount of VC. These reactions require a certain amount of time, such that an indication of the VC content does not show until 5 minutes after dosage. The detection limit of this method is 1 ppm.

Ultrared Instruments [1]

Ultrared instruments represent an effort to improve the selectivity on the scale of trace concentrations. Two types can be distinguished: the Uras-type which does not work dispersive but (which uses) the test gas as reference gas and those instruments which operate dispersive with prisms and filters.

Gas-Chromatography

The highest degree of selectivity (is) achieved by gas chromatography which, however, can only measure continuously. (This method) combines the advantages of selectivity with high accuracy and sensitivity. Here the flame ionization detector is hooked up with a coupling unit which allows the classification of the test specimen by boiling point and affinity of its components. These are introduced one by one by means of the carrier gas into the detector which analyses

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1) Translator's Note: Infrared (?)

them quantitatively. Samples can be taken from any areas or extracted from exhaust ducts.

Detection Limit and Selectivity of Various Methods for the Determination of Vinyl Chloride in Air			
Instrument	Detection Limit (ppm Volume)	Selectivity	Interference Factors
Drager Capillary	50	Limited	Unsaturated hydrocarbons
FID	1	None	All Hydrocarbons and Ammonium
Ionoflux Type	1	Slightly Limited	Halogenated hydrocarbons
Ultrared (Uras-type)	5	Limited	Dusts, Vapors, Carbon Dioxide
Ultrared (Dispersive)	0.7		
Gas-Chromatography	0.2	Available	Minimal

VC contents in food products and in PVC can be defined in (a) similar fashion. Food products such as mineral water, wine vinegar or alcoholic beverages, as well as molten fats and oils are introduced with a hypodermic needle in the dosage section which is heated to 100°C, whereby volatile portions evaporate

immediately and are carried away by the carrier gas.

For testing of PVC, a solid which can not be injected, a solution of the polymer (such as in tetrahydrofuran) is required as a first step. Obtainable detection limits for VC are 0.2 ppm in air (volume ratio),[1] 0.2 ppm (weight ratio) in water and fat based food products and 1 to 5 ppm (weight ratio) for PVC.

Sampling

Correct sampling is very important. Sample size must be large enough to show a representative cross section of the total. The usual methods to obtain such an average sample include (blending,) dividing, homogenizing and the like. In the case of PVC in powder form it has to be recognized that particles which lie near the surface (volatilize) faster than those which are located in the center of the bulk.

VC-REDUCTION

Residual monomer which after polymerization (and flashing) remained in the PVC typically volatilizes (to a large extent into) the atmosphere during drying, classifying and air conveying operations. The intensive efforts by the industry to operate at low emission and

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1) PPM (volume ratio) and (weight ratios) differ in the determination of Vinyl Chloride traces in air numerically by a factor of 2.6. PPM (volume ratio) represents the (volume) ratio of Vinyl Chloride gas to total gas PPM (weight ratio) on the other hand is the weight portion of Vinyl Chloride of the total weight. The density of Vinyl Chloride gas is approximately twice that of air.

loss levels concentrate on achieving a radical (volatilization) method applied to a system which is hermetically closed to the ambient atmosphere, and which is expected to further lower the VC content in commercial PVC.

The administrative regulations for the Environmental Protection Law - the so called"Technical Direction Air"- imposes a strong restriction on VC contamination allowed to the environment with a maximum of 150 mg (VC) per m^3 exhaust (volume) with a flow rate of 3 kg per hour.

In view of the measures to be taken at all processing operations, knowing the concentration of VC in the various types of (commercial) PVC should receive considerable attention. These VC contents are presently still to be used as guidelines for the protection of the worker in processing areas. It is self-evident, however, that this can only be a temporary stop gap measure. By consensus among PVC producers, the solution to the VC problem can only be achieved through a drastic lowering of (the) VC content in (commercial PVC) or compound.

Present Reference Values

An opinion on the (content as experienced today) residual VC has to remain very vague, however, unless it refers to specific types of PVC. Nevertheless some guideline values shall be given as follows:

With emulsion PVC a significant factor is whether it is a fine or coarse grain type. Finely sprayed emulsion PVC contains a maximum of 10 ppm VC, a typically level is 2 to 7 ppm. Coarsely sprayed emulsion PVC generally contains 150 to 200, maximum approximately 250 ppm. Special grades such as used for

paste formulations contain a maximum level of approximately 70 ppm, typically however, around 20 ppm VC.

The range of applications for suspension PVC is much larger than that for the other two types of PVC. Correspondingly many different grades of suspension PVC are being produced to satisfy market demands. General comments on the VC content are difficult, as there is no correlation to any single property. An attempt to reduce the VC content categorically leads to a change in the overall properties of PVC. Therefore only close cooperation between processor and producer makes the attainment of a minimum VC content possible with a simultaneous maintenance of property differences. It follows, that presently only a range of VC content between 10 to 1,000 ppm for suspension type PVC can be postulated. These values could be higher for specialty types. The supplier can provide pertinent information.

Typically residual VC contents for bulk PVC fall in the range of 100 to 1,000 ppm. Bulk PVC degasses particularly quickly. Therefore, generally speaking, VC contents are significantly lower at the processor level.

These broad indications alone show that a general statement on the monomer content is simply impossible. The required differentiation makes a direct dialogue for the determination of exact levels between producer and processor indispensable.

In addition, the above indicated residual VC contents have resulted from testing of freshly produced PVC. Further degassing occurs during the various shipping steps and storage in bags or silos. It is therefore impossible to make binding

statements on the residual amount of VC in existence at the time of delivery to the processor. Only maximum values could possibly be indicated.

Likewise a PVC producer can not guarantee a specific minimum storage time with corresponding VC reduction. The reason for this is, that all PVC producers maintain a lower number of production lines than the number of grades they offer. Several grades are therefore successively produced on one line. It follows that production has to be in large lots and shipments have to be equalized over constantly and significantly changing inventory levels. As a consequence the shipment of a mixture of freshly produced (in conjunction with) already several weeks aged PVC is unavoidable.

Future Considerations

All PVC producers (are undertaking) intensive efforts to develop new processes which in spite of technological difficulties will allow a further, significant reduction of residual VC contents.

Pilot plant know-how is already available. Much work is presently (being) done in scaling up to (commercial) PVC production quantities.

Design, ordering, delivery and installation of new equipment require time however.

Finally, as experience shows, time is also required for a legislative examination and approval of new processes.

Overall, there is no doubt, that in time we will be successful in upgrading production processes to the extent that health hazards can be eliminated in the future.

THIS IS PVC

Manufacturing

Polyvinyl Chloride is produced from Vinyl Chloride by polymerization. Commercial polymerization processes are classified as follows:

Emulsion Polymerization

Suspension Polymerization

Mass or Bulk Polymerization.

Emulsion polymerization is the oldest process; here the combination water/ Vinyl Chloride is transformed into a stable emulsion by the addition of emulsifiers or soaps (approximately 2%) and under agitation. Polymerization occurs inside so-called "soap micelles" with the aid of water soluble catalysts such as Hydrogen Peroxide or Potassium Persulfate. Surfactants such as used today in detergents, are added as emulsifiers. The resulting latex is converted to finished product by precipitation and spray or rotary drying.

The suspension polymerization process entails the dispersion of monomer droplets in water through intensive mixing and (through) ↓ the addition of suspension stabilizers. Polyvinyl Alcohol and derivatives of cellulose (act as suspension stabilizers) ↓ which have the task to further droplet formation and to prevent sticking of the individual polymerization particles. The reaction is initiated by Vinyl Chloride soluble catalysts. The resulting PVC is separated from the water phase by (a centrifugue) ↓ or decanting and dried.

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Mass or bulk polymerization of Vinyl Chloride with activators is accomplished without solvents or dispersants. The main portion of the polymerization proceeds in a powdery state, whereby agitation and heat transfer present special technical problems. From the point of view of processing technology, the mass process shows several advantages over the previously explained processes. Drying of the product is not necessary. Mass PVC is also completely free of additions such as emulsifiers and protective colloids. Catalyst residues are the only contaminants. The PVC particle is very porous which favorably affects its processability.

Properties

Hardly any other plastic material shows the wide range of application possibilities of PVC. This is not only made possible by the various conversion processes but also by the availability of a wide variety of raw material constituents and processing aids.

Polyvinyl Chloride's properties are based partially on its chemical composition, its structural characteristics and the various polymerization techniques, and partially on the effects of certain additives, which influence the processability and application of the pure raw material. This material is characterized by parameters such as the K-Value, particle shape and particle size distribution.

Particle shape, size and construction influence important product characteristics. They have an influence on bulk density, flowability, and plasticizer absorption and frequently have a bearing on which compounding

and conversion processes are to be chosen. A particle with good flow characteristics shows advantages (for pneumatic conveying and hopper) ↓ feeding (to processing) ↓ equipment. A high bulk density has a favorable effect on the throughput in extrusion, injection modling, or mixing operations. The production of dry blends requires a porous particle construction (with high plasticizer absorption) in conjunction with good flowability of the PVC powder. The viscosity characteristics of PVC paste formulations are among characteristics which can be influenced by the polymerization technique. (Different) ↓ Paste PVC's of the same K-Value, homogenized with the same amount of the same plasticizer could under the same temperature conditions and residence time lead to completely different viscosity and flow properties.

Nonplasticized compounds show good electrical properties. PVC can be formulated (to) ↓ transparent or opaque compounds.

Nonplasticized PVC is resistant to dilute or concentrated acids and bases, mineral and plant oils, alcohols and aliphatic hydrocarbons.

Rigid PVC formulations show good weathering properties, if suitable stabilizers and pigments are chosen. Flexible PVC is generally less weather resistant than rigid PVC.