

VINYL CHLORIDE MONOMER PROBLEM

IN JAPAN

July, 1974

JAPANESE PVC ASSOCIATION

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VVC 000006089

JAPANESE PVC ASSOCIATION

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VCM/PVC SITUATION IN JAPAN

I. VCM/PVC Industry

In Japan the VCM/PVC industry commenced the commercial production in 1949 -- although small production has been made during the Second World War -- and since then the industry developed smoothly and especially very fast of late years. The production of PVC in Japan has become the second largest in the world coming after your production.

PVC has superior properties and is sold at reasonable price. Thus it is used for producing containers, wrapping film, electric insulation, pipes and a wide range of products. It has become an indispensable material for improving the people's daily livings.

The manufactures of VCM/PVC are all members of the Japanese PVC Association listed as on annex. The production and shipment to date are as shown on annex table.

The workers employed for the production of VCM/PVC is roughly numbered at 2,200, and those engaged in the molding and processing business counts to about 500,000.

II. Problem of VCM Exposure

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1. At the occasion of the 16th International Congress on Occupational Health, held at Tokyo in the autumn of 1969, reports were made by the American and Italian doctors on acroosteolysis of employees at VCM/PVC plants. And the cause of the disease was named as VCM.

In reply to proposal by the workforce, the Japanese PVC Association took immediate actions by conducting a medical survey putting emphasis on cleaning work in the polymerization reactors, and prepared a Guide to Vinyl Chloride Operation Manual for Safe Handling and Use.

Subsequently, each member company of the Association has adopted up until today prevention measures respectively in accordance with this handling manual and has been executing a special medical examination of employees.

Except 2 workers who were suspected of acroosteolysis at the 2nd medical survey in 1972, we have not found so far the above specific disease.

2. At the end of January 1974, a report from USA of a possible connection between angiosarcoma of liver -- a rare form of cancer, -- of VCM/PVC manufacturing employees, and occupational health and safety for exposures to VCM has caused a worldwide discussion.

As soon as obtained such information, the Association discussed on what action the industry should take. As a conclusion, though liver angiosarcoma has not been found so far in Japan, the Association decided to cope with the suspected problem positively understanding that not only the health and safety of the employees, but the trend of the question is a critical problem which may threaten the existence of the Japanese PVC industry, and will greatly affect the national economy.

3. Actions

The actions took to date by the Association are as follows:

3-1) The Labor Health Committee was organized inside the Japanese PVC Association as for discussing this VCM problem, and also Medical Group and Technical Group were established as the sub-committees.

3-2) Through discussion by the Labor Health Committee an Emergency Temporary Standard on Occupational Health and Safety for Exposures to VCM was published, and the following items were recommended to the member companies by the President of the Association.

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a) VCM concentration shall be maintained not more than 50 ppm under work environments where employees will possibly be exposed to in production of VCM/PVC.

b) In any work environment where exposure exceeds the 50 ppm, employees shall be provided, and shall use, protective devices.

The members are enforcing the measures in their plant as soon as possible.

Further, a Temporary Standard for Medical Surveillance was prepared and medical screening is under way in accordance to this Standard. Surveillance is conducted parallel to this on the death cause of the employees including the retired workers.

4. The historical VCM concentration in atmosphere of the Japanese VCM/PVC plants are estimated as follows:

- 1955	maximum	1000 ppm
1955 - 1965	"	100 - 500 ppm
1965 - 1970	"	50 - 200 ppm
1970 - 1973	"	50 - 100 ppm
at present	"	50 ppm

In connection with the cleaning work in a polymerization reactor where a high level exposure to VCM is suspected, there are very few workers appointed specially for such cleaning heretofore. In Japan high-pressure water-jet cleaning system is applied, and the time required for staying in the kettle for poly-cleaning is now extremely short.

The water-jet cleaning system has been adopted in Japan from 1965 and in 1970 -- the year after an information was introduced into Japan that acroosteolysis patient existed among poly-cleaners -- every plant applied the system.

In the early period each time the polymerization is terminated the kettle was water-jet cleaned, and then hand scraping was made by the poly-cleaner. At present due to development on the system, one hand scraping for a very short time is required only once for several batches of polymerization.

III. Problem of VCM Migration

In May 1973 VCM migration problem of PVC liquor bottle spread into Japan from the United States. The Japan Hygienic PVC Association -- composed of 300 companies who are from PVC resin manufacturers to the food producers -- performed analysis on liquor from the same bottle and detected no such migration.

Further investigations were made on food wrappings beside PVC bottle. It was made clear that such problem will not occur by correct molding and by improved production process. At present such actions are taken by all the manufacturers.

Production and Shipment of PVC

Year	Production (metric tons)	Shipment (metric tons)	End-Use Percentage (%)			
			Rigid Products	Plasticized Products	Electric Insulation, Flooring, and Misc.	Export
1954	21,960	19,672	18.3	62.0	18.1	1.6
1955	32,210	33,651	36.3	46.3	14.2	3.2
1956	55,852	55,954	38.6	44.0	15.4	2.0
1957	108,905	91,379	40.5	42.3	14.7	2.5
1958	91,160	103,055	33.1	38.9	14.9	13.1
1959	179,247	180,880	37.0	37.0	14.1	11.9
1960	257,561	254,221	41.1	35.8	14.1	9.0
1961	307,526	298,336	43.3	35.5	14.0	7.2
1962	303,144	309,191	41.5	38.1	12.4	8.0
1963	348,061	353,244	44.3	38.1	11.5	6.1
1964	473,376	473,363	47.4	34.5	12.0	6.1
1965	482,992	466,614	40.8	34.0	11.1	14.1
1966	489,664	501,588	45.0	34.0	11.0	10.0
1967	711,099	712,306	49.5	30.9	13.1	6.5
1968	941,778	935,833	51.1	29.3	12.3	7.3
1969	1,047,078	1,046,775	49.3	27.8	12.7	10.2
1970	1,162,058	1,137,758	48.8	27.4	12.1	11.7
1971	1,019,269	1,063,198	48.9	26.8	10.6	13.7
1972	1,079,248	1,125,002	50.8	26.6	9.9	12.7
1973	1,313,098	1,315,915	55.2	26.1	9.8	8.9

Source : Japanese PVC Association

Guide to Vinyl Chloride Operation Manual for Safe Handling and Use

September 1970

Japanese PVC Association

Contents:

1. Properties
 - 1.1 Important physical and chemical properties
 - 1.2 Toxicity
2. Engineering Control of VCM and PVC Manufacturing System
 - 2.1 Production
 - 2.2 Facilities
 - 2.3 Instalation of cleaning system for polymerization reactor such as high-pressure water jet cleaner
 - 2.4 Ventilating in polymerization reactor
 - 2.5 Ventilation of VCM handling area
3. Control for Handling and Use
 - 3.1 Transportation
 - 3.2 Storage
 - 3.3 Application
 - 3.4 Cleaning operation of polymerization kettle
 - 3.5 Leak and procedures
 - 3.6 Other operation notifications
 - 3.7 First aid
 - 3.8 Education and training
4. Medical Screaning
5. Other Protection Procedures

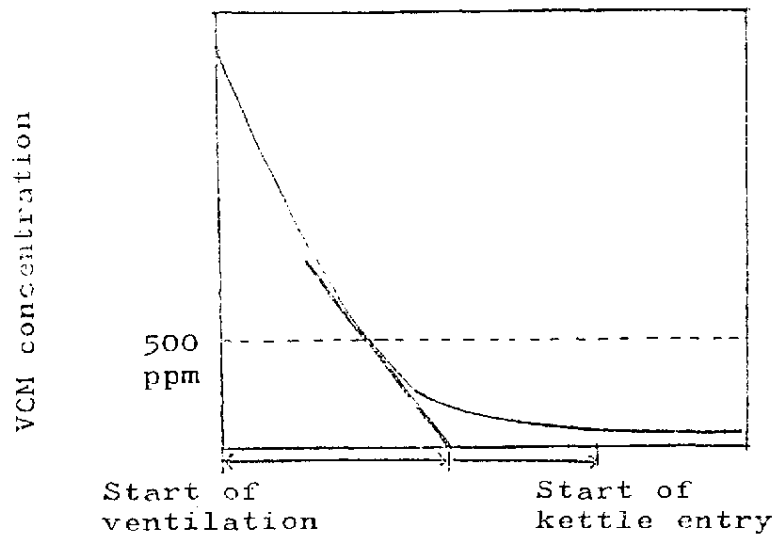
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3.4 Cleaning procedure in a polymerization kettle

- (1) Whenever the manhole of a polymerization kettle is opened, make sure not to inhale residual vinyl chloride monomer (VCM) gas since it flows out. For example, transfer slurry simultaneously when the manhole is opened or start exhauster immediately after opening of the manhole.
- (2) Before entering the reactor, wash the inside by high pressure water.
- (3) Turn off pipe lines of the reactor and disconnect motors without fail and lock switch board in the presence of a responsible person. Put up a sign of "Operator in the reactor".
- (4) Remove completely residual VCM gas in the reactor by water substitution or exhauster etc. to decrease gas concentration in the bottom part of the inside reactor below the permitted concentration.

In case exhauster is used, since the relation between residual VCM gas concentration in the reactor and degassing time is shown in the following figure, set up a degassing time 1.5 times as long as the required time for decreasing sufficiently the VCM concentration to arrive at equilibrium condition.

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Ventilation

Relation between degassing time
and VCM concentration in the reactor

Measure VCM concentration by one of
the following methods.

- (a) Kitagawa type detector
 - (b) Interference refractometry
 - (c) Gaschromatography
- (5) While cleaning of the reactor, always introduce large quantity of fresh air into the reactor to maintain VCM concentration below the permitted level. Also observe carefully to maintain it.
- (6) Use the following protective devices.
Store the protective devices in a specified storing place where a clear sign is put on to that effect. Check them periodically, at least once a week.
- (a) Protective glasses
 - (b) Protective gloves
 - (c) Protective clothing suitable to prevent skin contact such as long sleeve clothes

- (7) Employees engaged in reactor cleaning should wash face and hands after cleaning work and take bath or shower at the end of the shift.

4. Medical screening

The following points shall be checked up as to employees engaged in polymerization or other operation which may expose them to VCM.

- (1) At time of initial employment and once every year or more often (as for X-ray examination, once every two years)

Periodical examination shall be made to find whether the below mentioned items are detected or not.

- (a) Headache, head heaviness, tiredness, gastroenteric disorder, skin alteration, paralysis of fingers, pain and indisposition, arthritis, Raynaud syndrome and deformity or shortening of fingers.
 - (b) Urobilinogen and bilirubin in urine
 - (c) Semilunar marginal irregularity, transverse deformation, color-button phalanx detected by X-ray examination.
- (2) As a result of the above check-up, if subjective or objective abnormality is detected and a doctor finds them necessary, the following tests shall be applied.
 - (a) Liver function test (serum test on GOT and GPT)
 - (b) physical examination

Note:

Results of screening will be classified and health care will be followed accordingly. In the meantime, plant doctors shall take care of them.

June 1, 1974

To All Members

Subject: Emergency Temporary Standard on
occupational health and safety for
exposures to vinyl chloride monomer

Gentlemen:

We are pleased to inform you the following Emergency Temporary Standard which has been deliberated and decided at the 3rd Labor Health Committee on May 28, 1974. This is based upon the outline of the captioned Standard agreed at the 30th Board of Directors Meeting on May 21, 1974 to be adopted by the Japanese PVC industry.

Since institution of the Labor Health Committee we have been discussing the contents of this Emergency Temporary Standard. You may have already taken concrete measures along with the discussion. If not, we earnestly urge you to adopt the Standard to make perfection more perfect.

Emergency Temporary Standard

1. Vinyl chloride monomer (VCM) concentration must be maintained not more than 50 ppm under work environments where employees will possibly be exposed to in production of VCM and PVC.
2. In any work environment where exposure exceeds the 50 ppm, employees must be provided, and must use, protective devices.

With respect to the above 1 and 2, you are requested to enforce them as soon as possible.

3. Medical surveillance

This shall be decided by the Medical Subcommittee which is organized by plant physicians.

Incidentally, in the U.S. Proposed Rule was submitted to change labor environment standard from not more than 50 ppm of the temporary standard to a permanent level, no detectable level, virtually under 1 ppm. Reflecting such circumstances, our Labor Health Committee is planning to take the following measures in the next stage.

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- (1) Revision of work practice standard, especially the permitted level, taking account of results of continuing research as well as study results by the Medical Subcommittee.
- (2) Technical improvement to decrease monomer concentration under work environments and emission to the atmosphere and also technical improvement of monitoring system.

Sincerely,

JAPANESE PVC ASSOCIATION

M. Shimamura, President

June 12, 1974

Brief history of occupational
health and safety for exposures
to vinyl chloride monomer

In the autumn of 1969 at the 16th International Congress on Occupational Health held in Tokyo, doctors from the U.S. and Italy reported acroosteolysis of workers of PVC manufacture.

The Association immediately conducted a medical survey putting emphasis on cleaning work in a polymerization reactor and prepared a handling manual of vinyl chloride monomer under instruction from and the guidance of the Japanese Ministry of Labor.

Subsequently, each member company of the Association has adopted up until today prevention measures respectively in accordance with this handling manual and has been executing a special medical examination of employees. Except 2 workers who were suspected of acroosteolysis at the 2nd medical survey in 1971, we have not found so far the above specific disease.

Following to a report in the end of January by the B.F. Goodrich Chemical Co. in the U.S. of a possible connection between angiosarcoma of liver, a rare form of liver cancer, of PVC manufacturing employees and VCM exposures, occupational health and safety for exposures to VCM was caused worldwide discussion. In the U.S. Federal Resister dated April 5, 1974, Department of Labor billed a notice as an emergency temporary standard for exposures to VCM arising in process of VCM production, polymer production and molding.

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- (1) The temporary emergency standard requires that no employee exposure is permitted to levels of VCM concentration under work environments above a 50 ppm ceiling limit and
- (2) requires personal protective measures and equipment where exposure is greater than the 50 ppm level.

As soon as obtained such information, the Association discussed what action the industry should take. As a conclusion, though liver angiosarcoma has not been found so far by a medical examination in Japan, we organized Labor Health Committee in this April to cope with the suspected problem positively understanding that the trend of the question is not only a critical problem which may threaten the existence of the Japanese PVC industry, but also will affect greatly upon national economy.

The letter by Mr. Shimamura, president of the Japanese PVC association, shows activities so far and schedule for the future. There has been no such precedent before in Japan. Since there are many uncertain points, including relation between work environments and medical matters, the Association plans to dispatch a survey mission consisting of doctors and technical people.

June 10th, 1974

Sanitation of PVC food containers

In the United States some VCM was detected in whisky packed in PVC containers sometime ago. Subsequently FDA announced a ban against PVC containers used for alcoholic beverages as a provisional measure in May, 1973.

We, Japan Hygienic PVC Association, followed to the FDA announcement without falling behind.

As the results of our VCM analysis in SAKE, ardent spirits, and other relating foods, VCM was not detected in any case.

On the other hand, as the results of our research on tracing the VCM migration to its origin, it has appeared that by severely control on production process and by improvement of production equipment susceptible VCM migration into food can be minimized to non-detection.

As the consequence, it was consented to observe voluntarily its production method in the industries. And, it is being proceeded to form a system that no detectable VCM be remaining in food thereafter.

Japan Hygienic PVC Association

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Japan Hygienic PVC Association

—— its organization ——

CHAIRMAN

BOARD OF DIRECTORS

PROPAGATION OF RECOMMENDATION COMMITTEE

Propagation of the recommended standard.

Checking of the products in market.

PUBLIC RELATION COMMITTEE

Propagation of the Safety of PVC products standardized in accordance with positive list.

Issuing of the Associations report and technical service report, etc.

RESEARCH COMMITTEE

Research of shipping statics as plastic food packaging materials.

TECHNICAL COMMITTEE

Researching of the regulation related to the recommended P.L.

Collection and arrangement of technical report at home and abroad.

COMMITTEE ON BUSINESS AFFAIRS

Negotiation and liaison with the related official Agencies and referenced Associations.

Management of General affairs

VVC 000006105

VCM Migration from PVC Bottles

June 1, 1974

Japan Hygienic PVC Association

Experiment

1. VCM migration into alcoholic solvents with use of PVC resins containing different levels of residual VCM, PVC bottles containing various levels of residual VCM (1~ca. 20 ppm) were moulded.
Filled with 20 % and 50 % alcoholic solutions into the PVC bottles, and the filled bottles were kept at 50°C for 4 weeks.
And then, the quantity of migrated VCM into the alcoholic solutions and the migration rate of VCM were estimated from the following VCM analysis data :

Table 1 describes the data of 50% alcoholic solution, at 50°C, for 4 weeks.

Table 1

	bottle weight (gram)	bottle volume (ml)	VCM in bottle (ppm)	VCM in solution (ppm)	VCM migration rate from bottle (%)
No. 1	20	200	1.1	0.02	20
No. 2	20	200	1.6	0.03	19
No. 3	27.6	400	2.8	0.07	37
No. 4	20	200	3.5	0.07	20
No. 5	13.3	100	8.8	0.40	32
No. 6	13.3	100	19.0	0.82	30
No. 7	20	200	23.0	0.56	24

(Average 26%)

Table 2 describes the VCM migration rates into 20% alcoholic solution and sake from PVC bottles containing various levels of residual VCM by the same manner as in Table 1 .

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Table 2

solution	bottle weight (gram)	bottle volume (ml)	VCM in bottle (ppm)	VCM in solution	VCM migration rate from bottle (%)
50% alcohol	13.3	100	2.4	0.05	15
"	13.3	100	8.8	0.21	18
"	13.3	100	19.0	0.48	19
sake	13.3	100	2.4	0.05	16
"	13.3	100	8.8	0.19	16
"	13.3	100	19.0	0.48	19

(Average 17 %)

From Table 1 and 2, in thinking of Japanese spirits, as the tested condition (at 50°C, for 4 weeks) is thought to have equivalent extraction effect to one year storage at room temperature, picking up the data of 50% alcohol solution in Table 1 out of the above data for the sake of more safe, and it was thought the average 26% migration rate should be reasonable for the time being.

2. Residual VCM content in PVC compound and bottle

It can be estimated the VCM migration amount into spirits from PVC bottles in referring Table 1.

In addition, to know of VCM behaviour on the line from PVC compounding process to bottle production, we analyzed VCM content in bottles made from PVC compounds containing various levels of residual VCM ranging from 1.7 to 23 ppm.

Table 3 shows the VCM analysis results, and the VCM transference into bottles was found average 78 %.

Accordingly, residual VCM in PVC bottles appeared to be predominantly determined at the stage of compounding process.

Tabl 3

	VCM in PVC compound (ppm)	VCM in PVC bottle (ppm)	Residue percent (%)
No. 1	1.7	1.3	77
No. 2	2.8	2.4	86
No. 3	15	12	80
No. 4	21	15.5	74
No. 5	2.8	2.4	86
No. 6	12.5	8.8	70
No. 7	23	17	74

average 78 %

Control method for VCM migration into PVC bottled food at
compounding process

PVC blow bottles are made by PVC bottle manufacturers with PVC powder compound supplied by PVC compounders. And, food is filled into the PVC bottles at the end.

From the experiment results shown in the previous sections, if the ratio A (weight of contents versus weight of PVC bottle) is fixed, in compounding process, we will be able to predict and control the VCM migration amount into food from PVC bottle.

In the following equation :

- A : ratio of weight of contents / weight of bottle
- k : VCM residue (%) from compounding process to bottle blowing process.
- f : VCM migration rate from PVC bottle into bottled food.

$$\text{Residual VCM amount in PVC compound} = \frac{\frac{X}{100} \times \frac{A}{100}}{\frac{k}{100} \times \frac{f}{100}}$$

Accordingly, to keep x - value below 0.05 ppm ;

In case of spirits, supposing A=10, k=80%, f=30% are

$$\text{fixed ; } \frac{0.05 \times 10}{0.8 \times 0.3} = 2 \text{ ppm (maximum VCM amount in compound)}$$

In this supposition, A=10 is rather particular case.

It is thought in general A=20 should be more common.