K-1711-Coojp V

IUPAC APPLIED CHEMISTRY DIVISION

Commission on Food Contaminants

1975

R&S 135181

Project No. 1: Collection of information on Food Contaminants derived from Food Packaging

Part 1: Vinyl Chloride in the Packaging Material

1) Introduction

During 1973 increasing concern was expressed about possible carcinogenic and other effects of vinyl chloride (VC). The practical implications include

a) the health of industrial workers exposed to VC during manufacture and processing of PVC,

b) the migration of VC, whose presence in PVC has been unequivocally demonstrated, into the atmosphere during processing,

c) the migration of VC into food and drink packaged in PVC containers.

A careful literature search over the last years revealed that most interest has been given to occupational hazards (points a and b) whereas data on non-occupational exposure (point c) are relatively scarce. According to the objective of the project this report deals exclusively with VC in packaging materials and its migration into the packed foodstuffs.

/...

Most of the data given in this report emerged from investigations performed in the author's laboratory and have not been published up till now. To enable a reasonable interpretation of the data the methods for analysis are described in detail.

2) VC in the packaging material

In a technical report of WHO (1) the content of VC in food packaging material was summarized as follows:

a) bottles generally contain less than 100 ppm and a level below 30 ppm is now more usually observed,

b) rigid film generally contains less than 10 ppm and a level of less than 1 ppm is often observed,

c) flexible film generally contains less than 1 ppm and a level below 0,2 ppm is usually observed.

According to our analyses we observed three periods depending on the effort the manufacturer have undertaken to decrease the VC content.

2.1. PVC-films of former production charges (1. period)

In the investigation of 80 PVC-films of former production charges (up till approx. June 1974) the frequency distribution of the VC-content was found to be as shown in the following table. As can be seen from this table, the VC-content mostly varied between 200 and 400 ppm. These PVC-films were made of raw materials with high VC-concentrations. Sometimes VC-concentrations of more than 1000 ppm were found in powdered PVC.

/...

VC-content of PVC-films of former production charges

VC-content [ppm]	< 50	50-100	100-200	200-300	300-400	> 400
Number of films	2	12	15	23	24	4

2.2. Transitional stage (2. period)

Immediately after discussions about the possibility of monomeric VC being detrimental to health had started, considerable efforts were made on the part of the PVC-processing industry to reduce the VC-content of PVC-films drastically.

In Fig. 1 the reduction of the VC-content during processing is illustrated, starting from powdered PVC with a VC-content of over 1100 ppm. By hot mixing at different temperatures (50, 75 or 100°C), cold-mixing, extrusion and in the film-making process the VC-content of the final product can be reduced to 85, 30 and 15 ppm respectively. This confirms the finding of the Verband Kunststofferzeugende Industrie e.V. (2) that increased processing temperatures reduce the VC-content of PVC.

During the transitional stage PVC-films were made, containing generally less than 50 ppm VC and only in exceptional cases up to 100 ppm VC. At the same time successful attempts were made by the PVC-manufacturing industry to reduce the VC-content in the PVC starting materials. As can be seen from the next table, it was now possible for the processing industry to use powdered PVC containing less than 50 ppm VC.

VC-content of PVC-powders

VC-content [ppm]	< 20	20-50	50-100	> 100
Number of measurements	17	7	4	1

2.3. PVC-films with a low VC-content (3. period)

After all the difficulties had been surmounted, it was now possible to make PVC-films with a low VC-content. Of the charges produced between December 1974 and May 1975 a total number of 776 films were analysed. With a few exceptions the VC-concentrations were less than 5 ppm.

VC-content of recently produced PVC-films

VC-content [ppm]	< 0.1	0.1-1.0	1.1-2.0	2.1-5.0	5.1-10
Number of films	380	308	53	32	3

From these values it is obvious that the PVC manufacturing and processing industries have made great efforts to reduce the VC-content of their products and that the production of PVC-films with VC-concentrations $\leq$ 10 ppm is now technically feasible.

3. Migration of VC into simulants and packed goods

3.1. Simulants

To investigate the relationship between the VC-concentration in the packaging material and the VC-content in the packed product, migration tests were carried out using the synthetic fat simulant HB 307*). HB 307 is a mixture of synthetic triglycerides. The

/...

*) HB 307 in constant and defined composition is delivered by: HATEC, Gesellschaft für naturwissenschaftlich-technische Dienste mbH, 2 Hamburg 50, Behringstraße 154.

fat simulant HB 307 permits the determination of the migration of packaging material components into fatty food under standard conditions, and with a high degree of accuracy. The technique applied has been described in detail by K. Figge and J. Koch (3).

The table below shows the VC migration values for a PVC-film with a VC-content of 60 ppm at different temperatures (20°C and 40°C) as a function of time. From these values it can be seen that during storage at 20°C the VC content in the simulant increased continously. At 40°C, however, the migration reaches a maximum, after which the VC content slowly decreases again.

VC-migration from a PVC-film containing 60 ppm VC into HB 307

Storage temperature [°C]	VC-migration $\mu g/dm^2$ after 10 days	20 days	40 days	80 days	160 days	VC-content of the film after 160 days [ppm]
20	5	8	15	29	45	14
40	18	29	60	57	51	0.7

In the calculation of the migration values ($\mu g/dm^2$) the following factors were taken into account: contact surface between PVC and simulant, weightof simulant and VC-content in simulant after storage.

In the conversion of the migration values into the VC-content in the packed product, the PVC-contact surface must be taken into account. Applying the rule of thumb that 1 kg is packed in 6 dm^2, the VC-content in the packed product stored at 20°C for 80 days works out at 0.18 ppm.

The following table and Fig. 2 show migration values for PVC-films containg different VC-concentrations (10 days, 40°C and 20 days, 40°C).

/...

VC-migration into HB 307 at 40°C

VC-content of the PVC-film [ppm]	VC-migration [µg/dm²] after 10 days	20 days
1093	340	520
833	300	420
799	230	390
571	170	280
438	130	240
60	18	29

Especially from Fig. 2 it can be seen that a linear relationship exists between the VC content of the packaging material and the VC content in the fat simulant.

For a given VC-limit for the packed product the maximum permissable VC-concentration in the packaging material can be calculated from this relationship. Putting the life of a PVC-packed product at 8 weeks plus a margin of 4 weeks, the value for 80 days/20°C (s. table) can be taken as a basis. Assuming the maximum permissable VC-concentration in the packed product to be 1 ppm, as recommended by Kunststoffkommission des Bundesgesundheitsamtes in Berlin, it can be calculated that the packaging material must not contain more than 300 ppm. If the VC-limit for the packed product is, for instance, 0.05 ppm, the maximum permissable VC concentration in the packaging material is 15 ppm.

Naturally, these values are only approximate values, as other factors, e.g. the contents/surface ratio, the wall thickness and hence the absolute VC-content in the packaging material also play a role.

The results reported in this chapter have been published by W.R. Eckert (4).

3.2. Food stuffs

Only few data are available on the content of VC in food. After up to three year's storage in miniature PVC bottles, gin and whisky contained 0,57 and 0,62 ppm of VC respectively (1).. This led US Food and Drug Administration to the proposal to ban the use of PVC bottles for alcoholic beverages.

The concentration of VC in orange squash and cooking oil have been found to be in the range of 0,01 to 0,08 ppm and 0,01 to 0,04 ppm respectively. The migration of VC from PVC bottles is dependent on the VC content of the bottle, the temperature and the duration of storage (1).

3.3. Hair care products

We examined various hair cosmetics and the corresponding PVC packaging materials:

Product	Storage period at room temperature	VC-content (ppm)	
		Container	Filled product
Shampoo A	30 weeks	51	0.14
Shampoo B	30 weeks	44	0.56
Shampoo C	30 weeks	15	0.08
Shampoo D	5 months	162*	0.6
Setting lotion 100 cc	30 weeks	156	2.8
Setting lotion 19 cc	30 weeks	32	0.25
Setting lotion V	30 weeks	< 1	< 0.05
Setting lotion Y	15 weeks	43	1.0
Setting lotion S	3 months	141*	1.2
Fön lotion	3 months	26*	0.2
Hair conditioner A	30 weeks	31	0.24
Hair conditioner B	30 weeks	18	0.17

* during filling operation

/...

The measured values show a clear relationship between high VC-content of the packaging and high VC-content in the packed product.

Alcohol-based products were observed to absorb particularly large quantities of VC.

3.4. Rinsing agents

The VC-contents of different packed products were between 0.3 and 2.5 ppm. It should be considered that rinsing agents are used in dilutions of 1 : 100 with water - corresponding to VC-values of max. 0.03 ppm.

Product	Storage period (weeks)	VC-content (ppm)
Household cleaner	35	0.4
	19	1.1
Dish washing fluid A	24	0.3
750 ml	17	0.3
Dish washing fluid B	31	2.2
750 ml	31	2.5
	21	1.0
Rinsing fluid for	29	1.0
automatic machines	29	1.3
	20	1.6
	20	2.0

Here we could only examine PVC-bottles of another delivery: Values between 60 and 465 ppm VC were observed.

4. Methods

A highly-sensitive method was required for the identification of VC. We decided to use the headspace technique and developed the following procedure in close accordance with the methods published by H. Puschmann (5).

4.1. Principle of the method

For the investigation of PVC-products 10% solutions are prepared in closed injection flasks. The solvent used is N,N-dimethyl acetamide (DMA) to which about 20 ppm of diethyl ether have been added

as internal standard. These solutions are thermostated at 50°C to establish the equilibrium. The subsequent gas chromatographic analysis of the gas phase is carried out with the GLC-automat Multifrakt F 40 (Perkin-Elmer). Packed goods are investigated analogously, whereby the ratio test material to solvent must be adapted for each packed good.

4.2. Reagents

N,N-dimethyl acetamide, a.g., Merck
diethyl ether, a.g., Merck
vinyl chloride, 99.9%, Baker Chemicals

Standard solution: Weigh 70 g of dimethyl acetamide into a 100-ml injection flask and add 140 mg of diethyl ether. Weigh exactly to 0.1 mg. Dilute this solution with dimethyl acetamide until the standard solution contains a defined amount of 2 µg ether / ml.

Calibration solutions: Starting from a 0.2% solution of diethyl ether in DMA, calibration solutions with defined amounts of VC and ether are prepared by introduction of VC and subsequent dilution with DMA.

4.3. Preparation of samples

Weigh 200 mg of PVC exactly to 0.1 mg into a 23-ml injection flask (accessories to F 40) and provide with a magnetic rod. Add 2 ml of standard solution with pipette and close flask immediately. Dissolve sample on a heatable magnetic stirrer while stirring vigorously. Finally the injection flask may be placed in a water bath at about 60-70°C. As soon as all polymer parts are dissolved, equilibrate the flask for 30 min at 50°C in the water bath of the F 40.

For the investigation of simulants or packed goods weigh 2 g of sample into injection flask and add 0.5 ml of standard solution.

/...

Add magnetic rod and close test tube immediately. Dissolve or homogenize sample in the warmth on a magnetic stirrer. Transfer sample to thermostate of the F 40. After 30 min the analysis can be performed.

4.4. Gas chromatographic conditions

The gas chromatographic analysis is carried out with the Multifrakt F 40. Up to 30 samples are placed in the sample changer thermostate at 50°C. After the equilibration time of 30 min, the analysis cycle is started.

Instrument conditions on F 40:

water thermostate	50°C
dosing line	150°C
dosing time	5 s
time of analysis	8 min (VC in PVC)
blowing time	0,5 min
re-entrance time	0,5 min
column	high-grade steel tube, 4 m in length, 2 mm int. diam., packed with 15% of Ucon LB 550-x on Chromosorb W-HP (100-120 mesh)
column temperature	60°C
carrier gas	20 ml N_2/min
retention times	3.45 min for VC 5.20 for diethyl ether

The chormatograms are evaluated quantitatively in a connected 3352-B data system (Hewlett-Packard).

Under the conditions given the cycle time is 9 min. After 22 analyses, the automatic course of analysis must be interrupted and the column temperature increased to 180°C to heat out the DMA. After this the oven temperature again is adjusted to 60°C and the automatic course of analysis restarted for further samples. The time of interruption due to heating-out is approx. 45 min. This

/...

time table of capacity only applies to the determination of VC in PVC. In the determination of VC in packed goods longer times of analysis (up to 20 min) must be taken into consideration since some of these products contain easily volatile components which may influence the course of analysis considerably.

4.5. Determination of the calibration factors

For the determination of the calibration factors volumes of 2 ml of the calibration solutions are placed in injections flasks and closed. The flasks are equilibrated in the F 40 and analysed under the conditions described above. The calibration factor F is calculated according to

$$F = \frac{A_{ST} \cdot C_{VC}}{C_{ST} \cdot A_{VC}}$$

A_{ST} = peak area ether

A_{VC} = peak area VC

C_{ST} = concentration ether (internal standard)

C_{VC} = concentration VC

The instrument-dependent calibration factor was determined to

$$F = 0.85$$

By addition of 200 mg of VC-free PVC to the calibration solutions it was ascertained that dissolved PVC does not influence the factor. The calibration factor only applies to the quantitative determination of VC in PVC. For the determination of VC in simulants or packed goods new calibration factors must be determined for each substrate because of the varying solubility of VC. Moreover, it has to be ascertained that the samples under investigation do not show peaks interfering with the evaluation. This can be done by the analysis of samples which have not been in contact with PVC.

4.6. Calculation of the results

The calculation is carried out according to

$$\text{ppm VC} = \frac{A_{VC} \cdot F \cdot C_{ST}}{A_{ST}}$$

The concentration for the standard C_{ST} is given in ppm, based on the amount of the sample weighed in.

4.7. Reproducibility of the method

In order to check the reproducibility of the method, two series of measurements were carried out. In each case we analysed 12 PVC-bottles of the same batch.

1st series of measurements (Batch 1)

single values: 7.0 7.0 6.6 6.8 7.0 7.3
6.9 7.3 7.0 7.1 7.2 6.6 ppm VC

mean value: 7.0 $\pm$ 0.23 ppm VC

2nd series of measurements (Batch 2)

single values: 0.62 0.56 0.57 0.60 0.58 0.57
0.55 0.57 0.58 0.56 0.61 0.60 ppm VC

mean value: 0.58 $\pm$ 0.022 ppm VC

4.8. Reference analyses

Basing on two examples it shall be shown, in how far the analytical results of different laboratories are in agreement.

-Example 1:

From Van den Bergh + Jurgens Ltd., Purfleet, Great Britain, we obtained PVC-bottles ex I.C.I. The results of analysis are

I.C.I.: 1.5 ppm VC

our laboratory : 1.4 ppm VC

/...

Example 2:

Two batches of PVC powder ex Chemische Werke Hüls, Germany (CWH) were analysed at CWH and in our laboratory. The following values were obtained:

	Content of VC (ppm)	
Batch	CWH	our laboratory
1	81	93
2	41	37

Since VC is an easily volatile substance, these differences in case of PVC powders can be explained already by different periods of sample preparation.

4.9. Detection limits

The detection limit of the method for VC in PVC-powders and PVC-packaging materials is 0.1 ppm. In simulants and packed goods the detection limits depend on the substrate. VC-contents as low as 0.01 ppm can still be identified accurately in simulants.

5. Conclusions

On 26 March 1974 a group of European toxicologists discussed the available toxicological and migration data on VC, with special reference to its carcinogenic potential. The meeting was held at the National Institute of Public Health, Bilthoven, The Netherlands.

As far as the problem of VC in packaging material is concerned the following conclusions were reached and agreed unanimously:

"At the present time there is no need to recommend that PVC should be banned as a food-wrapping material. The basis of this conclusion is that relatively high concentrations of VC (by inhalation) are needed to produce a carcinogenic effect. In comparison, the exposure of man from food intake is probably much lower. The further quantitation of this factor will be possible when oral studies on VC have been completed. Furthermore, it was noted that even less

toxicological data were available on possible alternative plastics for food wrappings. It was thought desirable and possible that PVC used for food and drink packaging should contain less than 20 ppm VC monomer. In effect this represents the establishment of a food grade of PVC, to ensure very low levels of contamination." (6)

In their 57th meeting the "Kunststoff-Kommission" of the "Bundesgesundheitsamt" in Germany declared that there is no evidence of any health hazard after consumption of food stuffs packed in PVC containers. In September 1974 90 days feeding trials, undertaken by the Dutch Zentralinstitut für Ernährungsforschung (CIVO-TNO) have been finished, whereby considerably higher amounts of VC have been applied orally than ever can be expected in food stuffs having had a contact with PVC. No toxicity was observed. Therefore the oral uptake of traces of VC in food stuffs has to be considered in another way than uptake of VC via inhalation (2).

Subchronic test only? Did not elucidate for carcinogenic potential.

The "Kunststoffkommission" has no objections if, as a precaution, the content of VC in food stuffs is limited to 1 ppm. The statement bases upon the feeding trials and the analytical results and may be changed after obtaining the results of long-term feeding experiments which have already been asked for (2).

Hamburg, 29 July 1975

G. Billek, W.R. Eckert u. C. Roloff

Unilever Forschungsgesellschaft mbH
Hamburg 50, Behringstraße 154

6. References

1. International Agency for Research on Cancer, Internal Technical Report No. 74/005, "Report of a Working Group on Vinyl Chloride", Lyon, June 1974.

2. Verband Kunststofferzeugende Industrie e.V. "VC/PVC : Maßnahmen zum Gesundheitsschutz", Frankfurt/M., November 1974.

3. K. Figge and J. Koch, Fd. Cosmet. Toxicol. II. 975 (1973).

4. W.R. Eckert, fette. seifen. anstrichmittel, in press.

5. H. Puschmann, "The analytical determination of the content of residual monomers in PVC and food simulants" lecture on the occasion of the PVC discussion meeting, Darmstadt, 26th/27th September, 1974.

6. G.J. Esch and M.J. van Logten, Information Bulletin B.I.B.R.A. 13. 246 (1974).

Fig. 2 Migration of VC into fat simulant HB 307
(6 dm^2 packaging area / kg product)

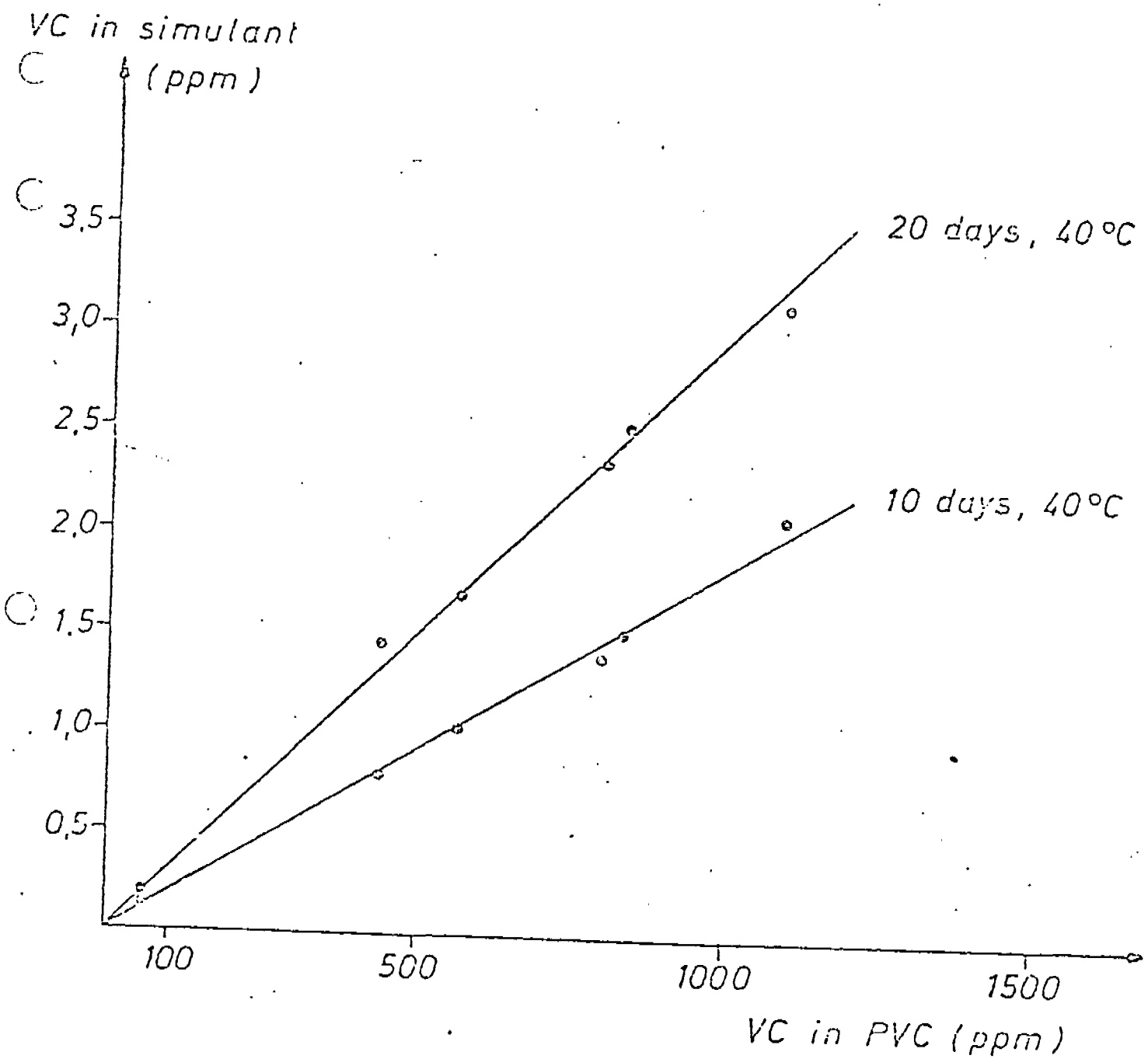
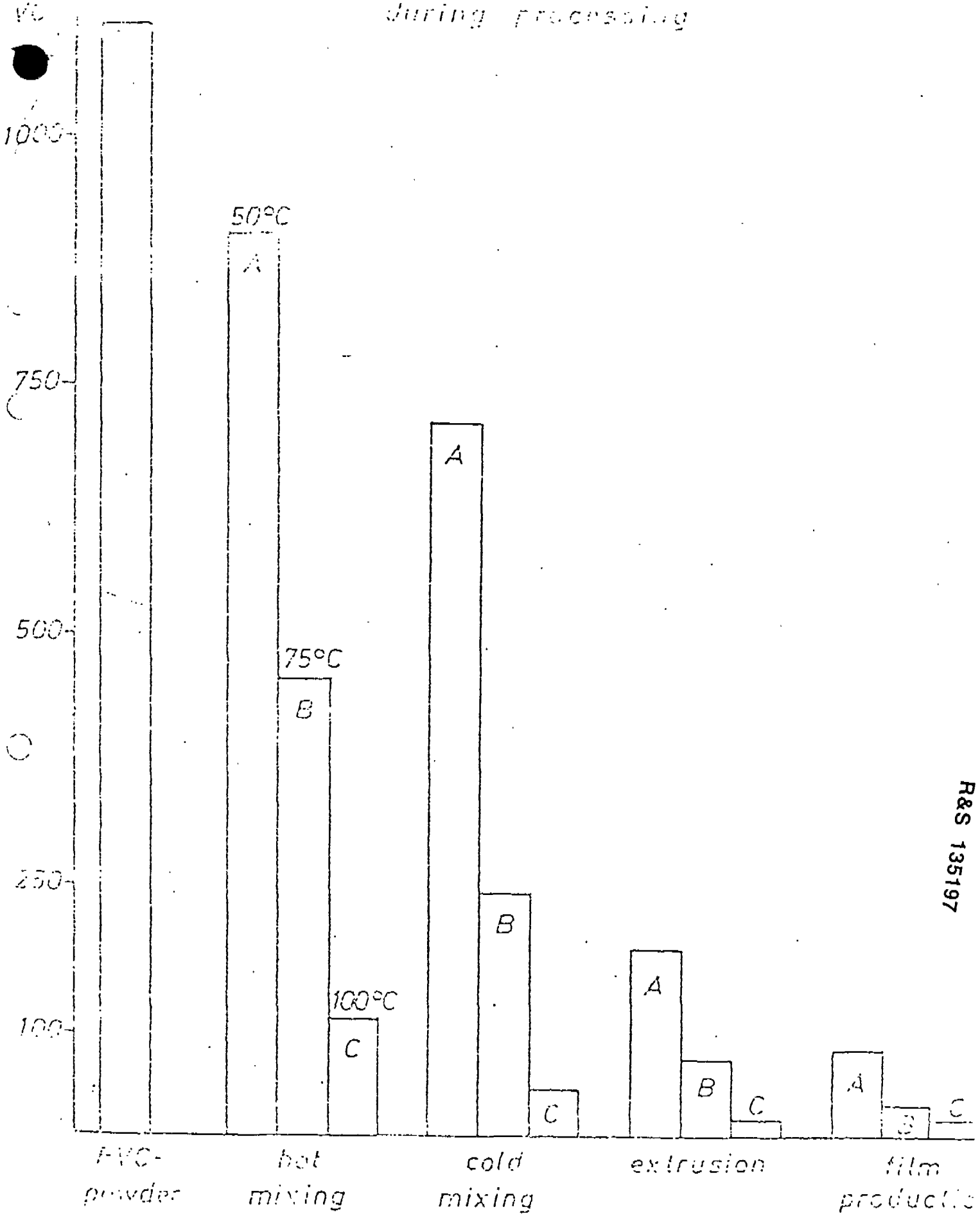


Fig. 1 Reduction of the VC content during processing



R&S 135197