



UNION CARBIDE CORPORATION
CHEMICALS AND PLASTICS

P. O. BOX 8004, SOUTH CHARLESTON, W. VA. 25303

0000813

Vinyl
Lit

1949

R&S 110905

UTH CHARLEST

Subject: Tribukh et al "Working Conditions and Measures for their
Improvement in Production and Use of Vinyl Chloride Plastics"
Gigiena i Sanit. (10) 38-44, 1949

Dear Bob:

The subject paper has been repeatedly cited as evidence of the early incidence of vinyl chloride and polyvinyl chloride toxicity. Other sources have stated that the author concluded that the toxic effects came from the plasticizers used. In an effort to clarify the discrepancy a copy of the original article in Russian was obtained and retranslated. The translation does not clearly attribute cause and effect to anything.

The authors' conclusions are as follows:

1. Organo chlorine compounds, hydrocarbons, hydrogen chloride and carbon monoxide are given off during the fabrication of PVC plastics.
2. These cause irritation of the mucous membrane in the upper respiratory tracts. Dusts and vinyl chloride resin vapors cause dryness and atrophy of the mucous membrane and cause chronic bronchitis over a long period of exposure.
3. Changes in worker upper respiratory tracts and hepatitis indicate the need for further health research.
4. Use of sovol (diphenyl chloride) as a plasticizer causes acne type skin injury to workers.
5. Protective clothing and showers should control the skin injury from sovol.
6. For cleaner work atmosphere the decomposition of PVC must be reduced and a rational ventilation system provided.

The authors are aware that diphenyl chloride and chlorinated naphthalenes (sovol and golowax) attack the parenchymal organs (parenchymal refers to distinguishing cells of an organ-not too clear). Severe toxic effects are acute and sub-acute yellow atrophy of the liver. They make no connection between this knowledge and the worker hepatitis.

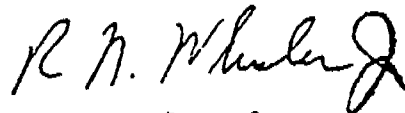
Other items of note are:

1. The specific process source of the PVC resin is not identified except that for shoe soles. Emulsion PVC is used for molding shoe soles. This type of PVC would be quite dusty and low in residual vinyl chloride monomer. Because of the widespread use of emulsion process PVC in Europe during this time it could be reasonably assumed that all the PVC used was made by this process.
2. The identification of potassium stearate as a stabilizer is in error. This is a soft soap probably used as a lubricant and non-stick agent. The stabilizer was probably some form of basic lead carbonate. No mention is made of pigments, fillers, etc. used which would contribute to dust and to toxic effects.
3. Neither diphenyl chloride (sovol) nor chlorinated naphthalenes golowax are good plasticizers for PVC. Dibutyl phthalate is the primary plasticizer. The other materials were probably added to the DBP to cheapen the cost or to get certain properties in the plastic.
4. The authors attribute the presence of organo chlorine compounds in the processing fumes to cleaved molecules of vinyl chloride (PVC-?) in different quantitative chain compound compositions. Boettner et al (Analysis of the Volatile Combustion Products of Vinyl Plastics) reports the major organic compounds given off during combustion pyrolysis of PVC are benzene and toluene with no condensible organo chlorine compounds.
5. Sampling and analytical techniques were not very sophisticated in 1949. Reactive gases such as hydrogen chloride and carbon monoxide could be accurately determined but the detection of hydrocarbon gases was based on the condensation of the material with ice or dry ice thus there could be no entrapment or measurement of very volatile hydrocarbons such as ethane, propane, butane or vinyl chloride. If organo chlorine compounds were truly collected and identified they must have resulted from the chlorine containing plasticizers in the plastic.

My own conclusion is that this study should not be related to any vinyl chloride or polyvinyl chloride health effects.

The translation was done by A. D. McCormick Company, P.O. Box 187, Dunbar, West Virginia 25064 not by Union Carbide Corporation.

Very truly yours,

A handwritten signature in dark ink, appearing to read "R. N. Wheeler, Jr.", with a stylized flourish at the end.

R. N. Wheeler, Jr.

RNWJr:ke

cc: J. W. Whittlesey

R&S 110907

PRODUCTION AND USE OF VINYLCHLORIDE PLASTICS.

Tribukh, S.L., Tikhomirova, N. P., Levina, S V., Kozlov, L. A.

Gigiena i Sanit. (10):38-44(1949)

The production of vinylchloride plastics and also the different goods prepared from them gained in the last decade considerable importance. In the meanwhile from hygienical point of view, it was little studied.

The basic raw material for the preparation of vinylchloride plastics is vinylchloride resin, which is prepared from vinylchloride, a colorless gas, condenses at 12 - 14° in liquid with a specific weight of 0,86 - 0,90. Vinylchloride, on its turn, is prepared by the reaction of gaseous decomposition products of petroleum vapors (vinyl) and gaseous chlorine. Subsequently, the vinylchloride condenses by using dichloroethane and is subjected to polymerization in autoclaves. In this way, polyvinylchloride resin is the product of vinylchloride polymerization. Due to the resistance to alkali, diluted acids, ethers, benzine and lubricating oil, polyvinyl chloride resin is used for the preparation of acidresistant fillers, fabrics for overalls, substituents to hides, etc.

At the preparation of various goods, the polyvinylchloride resin is plasticized with complex ethers of phthalic acid (dibutylphthalate), phosphoric acid (tricresylphosphate), mixture of diphenylchloride (sovol), or chlorinated naphthalenes (golowax). The selection of the plasticizer depends on the assigned use of the plastic to be prepared.

According to the data of the literature, vinylchloride belongs to weak narcotics. Its narcotic concentrations for humans are within the limits of 75 to 250 mg/l. According to the data by Petropavlovskii (1942), volatile substances, liberated, when vinylchloride resin and plasticizers are heated to 130-165° cause in animals under the condition of one single inoculation, depending on the concentration, the following phenomena:

irritation of the ocular mucous membrane, respiratory disorders, damage of the central nervous system, breakdown in the coordination of movements, and death, after appearance of asphyxic convulsions.

Sovol and golowax, introduced into vinylchloride plastics, as plasticizers, have general and local toxic effect. In their overall action on the organism, sovol and golowax are close to chlorinated fatty hydrocarbons. Basically they attack the parenchymal organs. Severe toxic effect takes place in form of acute, or subacute yellow atrophy of the liver. In the literature, cases with lethal outcome are described, caused by the toxic effect during the production with vinylchloride naphthalenes (golowax) and diphenyls (sovol). The local action of sovol and golowax causes acn -type skin eruptions and erythematous-vesicular dermatitis.

We studied the working conditions at the finishing of vinyl chloride plastics under factory conditions in a vinylchloride plastic plant, using vinylchloride plastics as substituent for hides and for insulation of electric wires.

Production of vinylchloride plastics:- In the vinylchloride plastics plant, the vinylchloride resin (a white powdery mass) is mixed with dibutylphthalate, or with sovol in mixing apparatus, at a temperature of 80-100°. Then, the compound is transferred onto rollers, the surface of which is heated to 130-160°V.

At the end of the rolling, the vinylchloride fabric is cut up in narrow tapes, which are further sorted and packaged in boxes.

R&S 110909

During the hygienical inspection of the vinylchloride plastic plant, the air of the working place was examined on its sovol-, organochlorine compound-, and hydrochloric acid vapor content. The obtained results are plotted in Table 1.

Table 1:- Organochlorine compound, sovol and hydrogenchloride content in the air of vinylchloride plastic plant

1 Название отделения	2 Место взятия пробы	3 Концентрация в мг/л	
		3a хлороорганические соединения, в том числе совола	3b хлористый водород
Подготовительное	8 В шкафу для подогрева совола	0,005	15 Не обнаружен
4	9 В середине помещения на уровне дыхания рабочего	0,003	"
5 Смешения и вальцовки	10 У смесителя во время смешения компонентов	0,06-0,08	0,025
6 То же	11 У смесителя во время выгрузки композиций	0,01-0,08	15 Не обнаружен
"	12 На рабочем месте вальцовщика	0,2-0,97	0,002
"	13 У стола для остывающего пластика	0,27	15 Не обнаружен
7 Сверловочное	14 У рабочего места сверловщика	0,005	"

1. Name of the department; 2. Place of the sample taking; 3. concentration in mg/l; 3a. organochlorine compounds, included sovol¹; 3b. hydrogen chloride; 4. preparation; 5. mixing and rolling; 6. the same; 7. drilling; 8. in the exhaust hood of the heated sovol; 9. in the middle of the chamber, at the respiration level of the workers; 10. at the mixer at the time when the components were mixed; 11. at the mixture, at the time when the components were discharged; 12. at the working place of rolling; 13. at the deck for the cooled plastic compound; 14. at the working place of the drill operator; 15. not detected;

In the air of the working places of the vinylchloride plastic plant, as one can see this from the data of Table 1, the concentration of organochlorine compounds fluctuated between 0,005 to 0,27 mg/l. In the preparation department sovol vapors formed at its heating, discharging and transportation. The concentrations of organochloride compounds, found in this place (0,005 mg/l) can be attributed, most likely, in great part to sovol.

¹ On account of the insufficiently developed method to determine separately organochlorine compounds, they were determined summarily.

t the mixers the organochlorine compounds were found in an amount from 0,01 to 0,08 mg/l, and in the working place of the rolling - from 0,2 to 0,97 mg/l.

In the product sorting department the organichlorine compounds, usually, did not exceed 0,05 mg/l. We detected hydrogenchloride only in the different samples in amounts, not exceeding thousandth part of milligram.

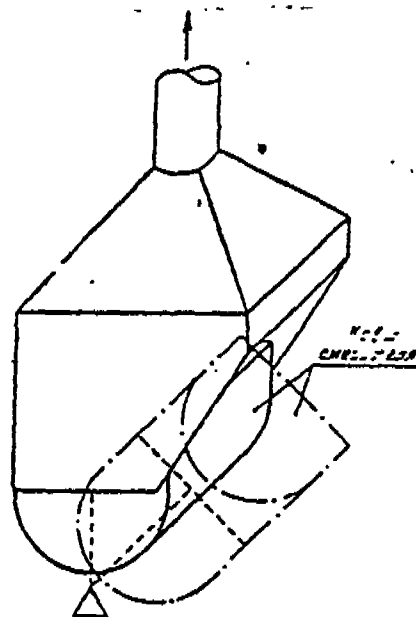
In connection with the use of sovol, soiling the skin with ingredients in the composition of which sovol was introduced causes serious danger. On the skin of the hands of the workers we found organochlorine compounds.

To fight the contamination of the air, the plant was mounted with influent and exhaust ventilation with automatic driving. The exhaust ventilation was constructed on the principle of local exhaust from the hoods, placed over the basic sources of gas evolution.

The efficiency of the ventilation, as this was demonstrated by the sanitary-technical inspection, was insufficient, on account of the fact, that the air-feed was carried out with a rate of only 7 - 8 m/sec on the level of the shoulders of the workers. The unpleasant sensation, caused by similar way of air feed, together with the infiltration and cooling of the compounds on the rollers forced the workers to overlay the damper of the sprinkling valves and already with this, the air current, escaping through the different leakages, decreased the work of the exhaust device, deviating the convective current, which got up from the rollers. Besides, the closing of the influx nozzle, disrupted the balance between the influx and the exhaust and attracted inorganized admission of contaminated air from the neighboring places.

R&S 110911

A significant defect of the ventilation system was the insufficient efficiency of the low-capacity hoods, arranged over the decks for the ready products and over the mixers. Much more effective are, according to our project executed orifices over the mixers in form of tents with open front wall (see the figure). At a productivity of 1 000 m³/hour these orifices practically completely localized the separation of noxious gas.



Scheme of the tentlike openings of the mixer.

Use of vinylchloride plastics as substituent for hides:- In the production of vinylchloride footwear, the basic raw material is polyvinyl chloride resin, which is prepared by the polymerization of vinylchloride in a water-emulsion method. The temperature of the decomposition of this resin is 130 - 150°. As plasticizer here dibutylphthalate and as stabilizer potassium stearate is used.

The compound for the sole is prepared by mixing textile scraps, saturated with dibutylphthalate, and vinylchloride resin in the mixer. The obtained compound is piled on the heater to 170 - 200° and rubbed through, after this with Vaseline in the press mold. The, in this way filled mass form is closed, it is maintained for a few minutes, and then is placed for a short time under the hot press.

R&S 110912

The composition for the upper footwear is obtained by mixing a determined amount of polyvinylchloride resin and dibutylphthalate in the mixer. The mass is kept there for aging 12 hours at a temperature of 70°. After the aging the compound is rolled at a temperature of 120-140° with the addition of potassium stearate. The vinyl chloride plastic compound, obtained after the rolling is rapped in textile and pressed at a temperature of 160°

The analysis of the air for noxious gas and vapor content in the plant of vinylchloride footwear production is plotted in Table 2.

Table 2:- Concentration of gases and vapors in the air of working places in vinylchloride footwear manufacturing plants in mg/l

Место взятия проб /.	1 Хлорорганиче- ские соединения					2 HCl			7 C (суммарно)			CO		
	6 концентрация в мг/л													
	3 миним. мг/л	4 максим. мг/л	5 средний	3 миним. мг/л	4 максим. мг/л	5 средний	3 миним. мг/л	4 максим. мг/л	5 средний	3 миним. мг/л	4 максим. мг/л	5 средний		
1а У вальцов . .	0,14	0,48	0,35	0,028	0,036	0,032	0,07	0,35	0,2	—	—	0,022		
1б У прессов . .	0,25	1,13	0,65	0,008	0,036	0,055	0,21	2,61	1,23	—	—	0,019		
1с В помещении сварочной	0,53	1,2	0,92	0,03	0,17	0,23	0,10	0,65	0,23	—	—	0,01		

1. place of the sample taking; 1a. at the rollers; 1b. at the press; 1c. at the welding place; 2. organochlorine content; 3. minimum; 4. maximum; 5. average; 6. concentration in mg/l; 7. total.

The organochlorine compounds, which evolve at the thermal finishing of vinylchloride resins, represent cleaved molecules of vinylchloride in different quantitative chain compound compositions. In the air of the working places at the manufacturing of vinylchloride footwear, we found these compounds in an amount from 0,14 to 1,2 mg/l. Here we found also vapors of hydrochloric acid in concentrations from 0,008 to 0,17 mg/l, hydrocarbon vapors (determined summarily) from 0,21 to 2,61 mg/l and carbon monoxide vapors within the limits of 0,01 to 0,022 mg/l.

The contamination of the atmosphere by organochlorine compounds and vapors of hydrochloric acid increases in proportion with the temperature increase at the heating during the different manufacturing operations.

The ventilation of the working place was carried out by means of a few exhaust devices, originally destined for local exhaustion. In spite of the comparatively high frequency of air exchange (10 - 20), the efficiency of the ventilation was insufficient. Its basic imperfection was the lack of local removal of the gas, evolved during the work at the pressing, rolling and welding of the footwear.

The hood over the welding working benches, usually used in this kind of production, was not efficient and could not be considered as a local exhaust device, because at the welding of the vinylchloride footwear, the gases evolved on the level of the knee of the seated welder, in the immediate closeness to his face. A more radical device in the given case is a vertical exhaust channel against each working place. The removal of the air can be carried out through orifices in the platform of the working bench, the upper part of which, thus, should be used as planar exhaust channel.

Satisfactory effect can be observed also in case of exhaust through a horizontal box, arranged on the surface of the working bench. The rate of suction through the exhaust orifices should not be less than 6 m/sec.

Use of vinylchloride plastics for the insulation of electric wires:-

In the factory, where vinylchloride plastics are used as insulating material for electric wires, the covering of the wires with vinylchloride envelope, is carried out on extruders.

During the time, when the vinylchloride plastic compound is dried in the drying chambers, and also at its fusion and at the discharge of the wires from the hot envelope from the head of the extruder, in the air of the working space we found the following volatile substances (Table 3).

Table 3

Место взятия проб 1.	Хлороорганические соединения 2		HCl		C (суммарно) 4		CO	
	3 концентрация в мг/л							
	минимал- ная 9	максим- альная 10	минимал- ная 9	максим- альная 10	минимал- ная 9	максим- альная 10	минимал- ная 9	максим- альная 10
У шприцмашин в зоне 5 дыхания рабочего . . .	0,003	0,1	0,001	0,06	0,3	0,6	—	—
Над проводом, покрытым 6 горячей пластмассой . .	0,14	0,65	Не обна- ружена	—	—	—	0,017	0,05
В середине помещения //	0,004	0,088	То же	—	—	0,11	—	0,02
Над сушильным шкафом 7	0,10	0,14	—	0,016	0,08	0,24	—	—

1. Place of the sample taking; 2. organochlorine compounds; 3. concentration in mg/l; 4. summarily; 5. at the extruder in the zone of the workers respiration; 6. over the wire, coated with hot plastics; 7. over the drying chest. 8. was not detected; 9. minimum; 10. maximum 11. in the center of the place.

In the composition of the volatile substances, evolved at the heating of the vinylchloride plastics, up to 120 - 140°, there is an organochlorine content of 0,003 to 0,6 mg/l, vapors of free hydrochloric acid from 0,001 to 0,06 mg/l, hydrocarbon vapors from 0,08 to 0,6 mg/l, and carbon monoxide vapors from 0,01 to 0,05 mg/l.

The ventilation of the plant was accomplished by means of exhaust hoods, arranged on the telescopic downstroke over each extruder head. The gases, evolving at the drying of the plastic compound in the drying chest and at the cooling of the vinylchloride wire after discharging from the extruder head, arrived in the atmosphere of the working places, maintaining in them a considerable concentration of toxic substances.

R&S 110916

Results of the medical examination of the workers:- A randomly selected group of workers in the inspected plant was subjected to medical examination. In the vinylchloride plant 48 men were examined, mainly roller workers. At the rhino-larynx examination, in a great number of the workers, in the upper respiratory tracts (in the nose, larynx, and trachea) white films of dust were observed, which were formed as a result of the mixture of dust with the mucus. These films were compact at the touch and could be removed from the surface of the mucous membrane only with difficulty. In 17 men hyperemia of the mucous membrane of the upper respiratory tract was found. Chronic bronchitis was detected in 13 men. As to the change in blood circulating organs, one must mention vascular hypotonia (90 - 100/45 - 50) in 13 men, moderate hypertonia in one, arterio-cardio-sclerosis - in 5. The condition of the gastro-intestinal tract was characterized in 10 examined workers by chronic gastritis and in 2 by chronic colitis. In 15 workers there were alterations in the liver in form of more or less pronounced hepatitis, accompanied in 2 examined workers by cholecystitis.

Regarding the blood, 29 examined workers had low hemoglobin count; one - 46%, 22 50-55%, and 6 56-60%. The blood picture and the ROE were without peculiarities.

One must pay attention to the skin diseases (acne, bleakheads), especially on the face, the neck and the chest, found in the examined group. The skin injuries were found not only on the face of those who were in contact with sovol, but also on those, who were not in direct contact with it, but were working in the same place. Evidently, the skin disease was caused by the action of sovol, when its vapor was sorbed.

In the chemical plant 25 female workers were examined, mainly those, working at the presses and welding with a long working record of 3 - 6 years in the said professions. In some of them, examined for ear - larynx different degree of hyperemia of the mucous membrane of the upper respiratory tract was observed, on its whole extent, or only on the organic parts. Chronic bronchitis was found in 5, mildly expressed emphysema of the lungs in 3 and remaining signs of pleurisy in 2.

As to the cardio-vascular system in 14 men vascular hypotonia (R/R 90 - 110/55-65) and in 4 mildly expressed hypertonia (R/R 140 - 165/80-85) was detected. Thudding sound of the heart, its enlargement and the data of the ECG: low T-wave of heart, not less than by 2 basic abduction and the roundness of the S - T interval, gave foundation, in some cases, to diagnose dystrophy of the myocardium.

In the examined group, in 6 workers hepatitis was diagnosed. At the same time, in some persons, simultaneously liver and stomach disease was detected. Not in one of the liver disease cases could we find in the anamnesis, or at the examination, signs of jaundice. Neither did we detect any bile pigment in the urine. In a considerable number of the examined workers small swelling of the liver, without characteristic pain and sensitivity at palpation was observed.

Analyzing the results of the medical examination, one must remark, that in a known part of the workers, changes in the upper and deeper respiratory tracts were detected. These findings are confirmed also by the data of the literature.

One must pay attention to the high percentage of skin injuries, which is, no doubt connected ethiologically to the action of sovol.

R&S 110917

-11-

The presence of hepatitis in some workers, in contact with vinylchloride resin and vinylchloride plasticizers deserves serious consideration. Therefore further dynamic observations on the state of the health of the workers, who are in contact with vinylchloride resin and its plasticizers are necessary, to prevent the development of severe liver damage.

R e s u l t s .

1. - Into the composition of volatile substances, which form at the thermal finishing of vinylchloride resins and plasticizers, during the manufacturing of organo-chlorine compounds, hydrocarbons, vapors of free hydrochloric acid and of carbon monoxide enter.

2. The action of these volatile substances are manifested in the irritation of the mucous membrane, mainly of the upper respiratory tracts; lengthy influence of finely dispersed dusts and vinylchloride resin vapors cause, besides, dryness and atrophy of the mucous membrane of the upper respiratory tracts, and is also responsible for the development of chronic bronchitis.

3. A considerable number of hepatitis among the examined workers, and also the change in the upper respiratory tracts, raise the question of the necessity for further dynamic research on the state of the health of the workers and to take a series of therapeutic-prophylactic measures, in particular by organizing heat and moisture* inhalation of drugs for the workers.

4. At the use of vinylchloride solvent, as plasticizer, on most workers acne type skin injuries, with preferable location on the face and neck, were observed.

5. For the prophylaxis of skin diseases at the work with solvent, the following complex sanitary measures have to be taken: 1) securing for the workers work underwear and outfit; 2) construction of sanitary showers

*) (alkaline)

with separate undressing for home and work cloths. At the sanitary passage, there must be a vapor chamber for the low temperature steaming of underwear and work outfit, at a temperature of 110-120°, for one hour. The plant should be equipped with wash basins with hot and cold running water.

6. For the sanitation of the atmosphere, it is necessary to decrease, as much as possible, the degree of vinylchloride resin decomposition at its thermal finishing. This must be attained by standardizing its heat resistance, and also by controlling the temperature when the rollers, the presses and other equipment are heated, not to exceed 120-130°.

Of extremely great importance is the rationally equipped ventilation system, calculated on maximum screening-off the source of gas-, vapor- and dust separation.

In connection with the fact, that in some factories the inflammation of the condensate was observed, which occurred in the exhaust ventilation tubes in contact with open flame, the exhaust apparatus must be protected by observing the conditions, adopted by the construction legislation for construction, designated for the mixing of inflammable gaseous mixtures.

241

WORKING CONDITIONS AND MEASURES FOR THEIR SANITATION
IN THE PRODUCTION AND UTILIZATION OF VINYL CHLORIDE PLASTICS

S. L. Tribukh, N. P. Tikhomirova, S. V.
Levin and L. A. Kozlov¹

Translation of: "Usloviya truda i merogriyatiya
po ikh ozdorovleniyu pri proizvodstve i ispol'zovani
khlorvinilovykh plasticheskikh mass," Arg. Sanit.,
Volume 10, 1949, pp. 38-45.

Over the last decade there has been considerable development of the production of vinyl chloride plastics and of various articles of these plastics. Only little study has been devoted to this production, however, from the hygienic standpoint.

R&S 110920

The basic raw material in the manufacture of vinyl chloride plastics is vinyl chloride resin, which is obtained from vinyl chloride, a colorless gas which condenses at 12-14° into a liquid having a specific gravity of 0.86-0.90. The vinyl chloride in turn is obtained on interaction of the gaseous products of decomposition of petroleum (vinyl) with gaseous chlorine. The vinyl chloride is subsequently condensed by use of dichloroethane and is subjected to polymerization in autoclaves. The polyvinyl chloride resin is thus a product of polymerization of vinyl chloride. Because of its stability toward the action of alkalis, diluted acids, alcohol, benzene, and lubricating oil, polyvinyl chloride resin is employed in the production of acid-resistant washers, fabrics for protective clothing, leather substitutes, and so forth.

In the manufacture of various articles the polyvinyl chloride resin is plasticized by esters of phthalic acid (dibutylphthalate), phosphoric acid (tricresylphosphate), and a mixture of chlorodiphenyls or chlorinated naphthalenes (Holowax). Selection of the plasticizer depends on the purpose of the plastic being manufactured.

According to data in the literature vinyl chloride is a weak narcotic. Vinyl chloride concentrations which are narcotic to man range from 75 to 250 mg/l. According to Petropavlovskiy (1942) the volatile substances evolved on heating of the vinyl chloride resin and plasticized resins to 130-165° cause the following effects in animals subjected to a single inoculation, depending on the concentration: irritation of the visible mucous membranes, impairment of respiration, affection of the central nervous system, impairment of coordination of movements, and death accompanied by phenomena of asphyxial convulsions.

The chlorinated diphenyl and Holowax introduced into the plasticized vinyl chloride resin as plasticizers have a general and local toxic effect. In their general effect on the organism the chlorinated diphenyl and Holowax resemble chlorine-substitution hydrocarbons of the aliphatic series. In the main they affect the parenchymatous organs. The course of severe intoxication is that of acute or subacute yellow atrophy of the liver. Cases have been described in the

¹Production Research Laboratory of the Institute of Labor Hygiene and Occupational Diseases of the Academy of Medical Sciences of the USSR.

literature of fatal termination in poisoning during production with chlorinated naphthalenes (Holowax) and diphenyls. The local action of chlorinated diphenyl and Holowax is manifested in skin affections of the acneform and erythematous-vesicular dermatitis.

We have studied the conditions of work with vinyl chloride plastics under plant conditions at a plasticized vinyl chloride resin shop, the resin being used as a leather substitute and for insulating electric conductors.

Production of chlorinated plasticized resin. At the chlorinated plasticized resin shop the vinyl chloride resin (a white powdered mass) was mixed with dibutylphthalate or with chlorinated diphenyl in mixing equipment at a temperature of 80-100°. The composition was then transferred to rollers the surface of which was heated to 130-160°.

At the end of the rolling process the sheet of vinyl chloride on the rollers was cut into narrow strips which were subsequently sorted and packed in boxes.

In inspection of the plasticized vinyl chloride resin shop the pair of the areas in which work was done was analyzed to determine its content of vapors of chlorinated diphenyl, organic chlorine compounds, and hydrochloric acid vapors. The results obtained are summarized in Table 1. As is to be seen from the data given in Table 1, the concentration of organic chlorine compounds ranged from 0.005 to 0.27 mg/l in the air of the production rooms of the plasticized vinyl chloride resin shop. In the preparation department chlorinated diphenyl vapors were liberated during heating, pouring and transporting of the resin. The concentration of organic chlorine compounds found in this room (0.005 mg/l) may with high probability be ascribed chiefly to the chlorinated diphenyl. Organic chlorine compounds were found in the mixers in an amount ranging from 0.01 to 0.08 mg/l, and at the roller operator's station from 0.2 to 0.97 mg/l.

In the sorting department the concentrations of organic chlorine compounds usually do not exceed 0.05 mg/l. Hydrogen chloride was found only in isolated samples, in amounts not exceeding thousandths of a milligram.

As a result of the use of diphenyl a serious danger is represented by the presence of conditions permitting contamination of the skin with ingredients forming part of the composition. We found organic chlorine compounds on the skin of the worker's hands at the end of the work day.

In order to prevent air pollution the shop is outfitted with forced air intake and exhaust ventilation. The exhaust ventilation is organized on the principle of local exhaust from hoods mounted above the main sources of gas evolution.

As was demonstrated by the sanitation engineering inspection, the effectiveness of the ventilation was inadequate because of the fact that the air was delivered at a rate of only 7-8 m/sec at the level of the worker's shoulders. The unpleasant sensations caused by this method of air delivery, along with the swelling and cooling of the composition on the rollers, forced the workers to cover the slide valve of the sprinkler pipes, and even when this had been done the streams of air escaping through various leaks impaired the operation of the exhaust

system, deflecting the convection flows rising from the rollers. In addition, closing of the intake pipes disrupted the balance between the inflow and exhaust and caused disorganized intake of polluted air from adjacent rooms.

TABLE 1. CONTENT OF ORGANIC CHLORINE COMPOUNDS, CHLORINATED DIPHENYL, AND HYDROGEN CHLORIDE IN AIR OF PLASTICIZED VINYL CHLORIDE RESIN SHOP.

Name of department	Place of sampling	Concentration, mg/l	
		Organic compounds, including chlorinated diphenyl ²	Hydrogen chloride
Preparation	Chlorinated diphenyl heating cabinet	0.025	None detected
	Center of room at level of worker respiration	0.003	" "
Mixing and rolling	At mixer during transfer of compositions	0.06-0.08	0.025
Same	At mixer during transfer of compositions	0.01-0.08	None detected
	At roller operator's position	0.2-0.97	0.002
	At plasticized resin cooling table	0.27	None detected
Drilling	At drilling operator's station	0.005	" "

Commas indicate decimal points.

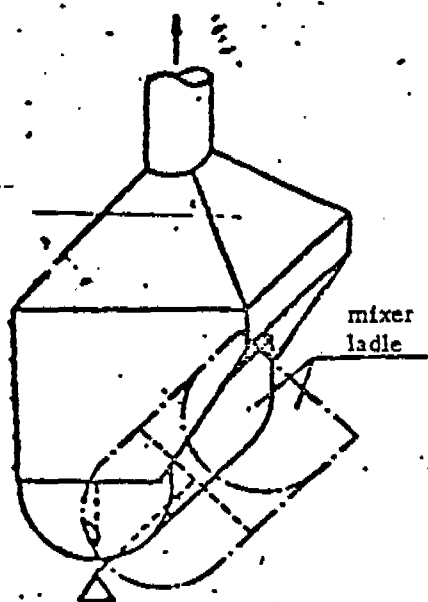


Diagram of Hood Cover of Mixer.

A serious defect in the ventilation system was represented by the inadequate effectiveness of the low-capacity hoods mounted above the finished product tables and above the mixers. Hoods above the mixers in the form of tents with the front wall open (see drawing) (produced on the basis of our design) proved to be much more effective. With a delivery of 1,000 m³/hour these hoods almost entirely localize the evolution of noxious gases.

Use of plasticized vinyl chloride resins as leather substitutes. The basic raw material in the production of vinyl chloride footwear is polyvinyl chloride resin obtained on polymerization of vinyl chloride by the water-emulsion method. The temperature of decomposition of this resin is 130-150°. The plasticizer employed in this case is dibutylphthalate, and calcium stearate serves as the stabilizer.

²Since the method of separate identification of organic chlorine compounds has not been adequately developed, here they were given a general identification.

The sole composition is prepared by mixing cloth scraps impregnated with tributylphthalate and vinyl chloride resin in a mixer. The composition obtained is placed on a mold heated to 170-200° and afterward smeared with vaseline. The mold filled in this manner is covered, held for several minutes and then placed under a hot press for a short time.

The composition for the uppers is obtained by mixing specific amounts of polyvinyl chloride resin and dibutylphthalate in a mixture. The mass is left here to age for 12 hours at a temperature of 70°. After the aging the composition is rolled at a temperature of 120-140° and calcium stearate is added. The plasticized vinyl chloride resin obtained after the rolling is transferred to fabric and pressed at a temperature of 160°.

The results of analysis of the air for its content of noxious gases and vapors in the vinyl chloride footwear shop are presented in Table 2.

TABLE 2. CONCENTRATION OF GASES AND VAPORS IN AIR OF VINYL CHLORIDE FOOTWEAR PRODUCTION SPACES, mg/l

Place of sampling	Organic chlorine compounds			HCl			C (total)			CO		
	Concentration, mg/l			Concentration, mg/l			Concentration, mg/l			Concentration, mg/l		
	minimum	maximum	average	minimum	maximum	average	minimum	maximum	average	minimum	maximum	average
At rollers	0.14	0.48	0.35	0.003	0.036	0.032	0.07	0.35	0.21	—	—	0.022
At presses	0.26	1.13	0.65	0.003	0.036	0.035	0.21	2.61	1.23	—	—	0.019
In welding room	0.53	1.2	0.92	0.03	0.17	0.23	0.10	0.68	0.23	—	—	0.01

Commas indicate decimal points.

The organic chlorine compounds evolved in the heat treatment of vinyl chloride resin are detached molecules of vinyl chloride in various quantitative combinations of their chain compounds. We found these compounds in amounts ranging from 0.14 to 1.2 mg/l in the air of the vinyl chloride footwear production rooms. Vapors of hydrochloric acid were also detected here, in concentrations ranging from 0.008 to 0.17 mg/l, as well as hydrocarbons (ranging from 0.21 to 2.61 mg/l (total determination) and carbon monoxide ranging from 0.01 to 0.022 mg/l.

Pollution of the ambient air by organic chlorine compounds and hydrochloric acid vapors increase with elevation of the heating temperature in various production operations.

Ventilation of the production areas was accomplished by means of several exhaust fans initially designed for local exhaust ventilation. Despite the relatively high air replacement frequency factor (10-20), the effectiveness of ventilation was found to be inadequate. The chief defect in it was the absence of local removal of liberated gases formed during treatment of the composition on the presses and rollers and in welding of the footwear.

R&S 110923

The hood installation above the welding benches usually employed in such production is not effective and may not be regarded as a local exhaust device, since during the welding of vinyl chloride footwear gases are liberated at the level of the knees of the seated welding operator in the immediate vicinity of his face. The most radical installation in this particular case is a vertical exhaust duct opposite each of the operator's positions. Air may be removed through an opening in the top of the bench, which in this case must be used as a blast exhaust duct.

A satisfactory effect was also observed with exhausting through horizontal ducts placed on the surface of the bench. The rate of removal through the exhaust openings must be no less than 6 m/sec.

Use of plasticized vinyl chloride resin for the production of electric conductors. At the plant at which plasticized vinyl chloride resin is used as an insulating material for electric conductors, the conductors are sheathed with vinyl chloride on extruders.

The following volatile substances are released into the air of the production room during drying of the plasticized vinyl chloride resins in the drying cabinets, and also while it is being melted and when the conductors emerge from the head of the extruder into the hot sheathing (Table 3).

TABLE 3.

Place of sampling	Organic chlorine compounds		HCl		C (total)		CO	
	Concentration, mg/l							
	minimum	maximum	minimum	maximum	minimum	maximum	minimum	maximum
At extruder in area of worker respiration	0.003	0.1	0.001	0.06	0.3	0.6	—	—
Above conductor sheathed in hot plastic	0.14	0.63	Not observed	—	—	—	0.017	0.05
In center of room	0.001	0.08	Ditto	—	—	0.11	—	0.02
Above drying cabinet	0.10	0.14	—	0.016	0.03	0.21	—	—

Commas indicate decimal points.

The volatile substances liberated on heating of plasticized vinyl chloride resin from 120 to 140° include organic chlorine compounds in amounts ranging from 0.003 to 0.6 mg/l, vapors of free hydrochloric acid in amounts ranging from 0.001 to 0.06 mg/l, hydrocarbons ranging from 0.08 to 0.6 mg/l, and carbon monoxide ranging from 0.01 to 0.05 mg/l.

Ventilation of the shop was accomplished by means of exhaust hoods mounted on a telescoping lowering device above each extruder head. The gases released during drying of the plasticized resin in the drying cabinet and during cooling of the plastic sheathing of the conductor after it emerges from the extruder head entered the air of the production room, maintaining considerable concentrations of toxic substances in this room.

Results of medical examination of workers. Sample groups of workers from the enterprises inspected were subjected to medical examination. In the plasticized vinyl chloride resin shop 48 persons, primarily roller operators, were examined. Rhinolaryngologic examination revealed a white film formed as the result of mixing of dust with mucus in the upper respiratory passages (nose, larynx, and trachea) of a large number of the workers. Such films were solid to the touch and it was difficult to remove them from the surface of the mucous membrane. Hyperemia of the mucous membrane of the upper respiratory passages was found in 17 persons. Manifestations of chronic bronchitis were found in 13 persons. Among the changes relating to the organs of blood circulation mention should be made of vascular hypotonia (90-100/45-50) in 13 persons, moderate hypertonia in one person, and arterial cardiosclerosis in 5 persons. The condition of the gastrointestinal tract was characterized in 10 of the persons examined by manifestations of chronic gastritis and in 2 manifestations of chronic colitis. In 15 persons there were changes affecting the liver, in the form of more or less pronounced hepatitis, which in 2 of the persons examined was combined with manifestations of cholecystitis.

As regards the blood, in 29 of the persons examined there were low hemoglobin figures: 46% in one, 50-55% in 22, and 56-60% in 6 persons. The blood formula and the erythrocyte sedimentation test exhibited no abnormality.

Attention is attracted by the fact that skin diseases (acne, comedones) were observed in the group examined, especially on the face, neck, and chest. Cutaneous affections were observed not only in persons coming in contact with the chlorinated diphenyl, but also in ones having no direct contact with it when working in the same room. The skin diseases apparently were caused by the action of chlorinated diphenyl absorbed in the form of vapor.

At the chemical plant 25 female workers were examined, chiefly press operators and welders, ones who had worked in this occupation chiefly for periods ranging from 3 to 6 years. Various degrees of hyperemia of the mucous membranes of the upper respiratory passages, over the entire extent of the passages for only over limited sections, were observed in some of these persons, who were examined by an otolaryngologist. Chronic bronchitis was detected in 5 persons, moderately severe emphysema in 3, and residual effects of pleuritis in 2 persons.

As regards the cardiovascular system, vascular hypotonia (R/R 90-110/55-65) was observed in 14 persons and moderate hypertonia (R/R 140-165/80-85) in 4. The thudding sounds of the heart, expansion of its limits, and electrocardiogram data: a lower T-wave of no less than 2 basic deflections and grounding of the ST interval, provided a reason in several cases for a diagnosis of myocardiac dystrophy.

Hepatitis was diagnosed in 6 persons in the group examined. At the same time affection of the liver and stomach simultaneously was observed in some persons. In none of the cases of affection of the liver were we able to find symptoms of jaundice in the anamnesis or on inspection. Nor were there any bile pigments in the urine. Slight enlargement of the liver, without the characteristic complaints and sensitivity to palpation, was detected in a large number of the persons examined.

In analyzing the results of the medical examination it is necessary to note that changes relating to the upper and deeper respiratory passages were detected in a certain number of the workers. These observations are also confirmed by data in the literature.

Attention is attracted by the high percentage of cutaneous affections, which from the etiological standpoint are unquestionably associated with the action of the chlorinated diphenyl.

Serious attention should be given to the circumstance of the presence of hepatitis in some of the workers coming in contact with the vinyl chloride resin and the plasticized resin. Thus further close observation of the state of health of workers coming in contact with vinyl chloride resin and the plasticized resins are required in order to prevent the development of serious affections of the liver.

Findings

1. The volatile substances formed when vinyl chloride resin and plasticized resins are subjected to heat treatment in production include organic chlorine compounds, hydrocarbons, vapors of free hydrochloric acid, and carbon monoxide.

2. The action of these volatile substances is manifested in irritation of the mucous membrane chiefly of the upper respiratory passage; protracted action by the highly dispersed dust and vapors of vinyl chloride resin additionally causes dryness and atrophy of the mucous membrane of the upper respiratory passages, and also contributes towards the development of chronic bronchitis.

3. The considerable number of cases of hepatitis among the workers examined, as well as the changes in the upper respiratory passages, raise the question of the need for further close observation of the state of health of workers and the taking of a number of therapeutic and prophylactic measures, particularly organization of warm humid (alkaline) inhalation of medicinal substances for workers.

4. With chlorinated diphenyl used as a vinyl chloride plasticizer, cutaneous affections such as acne, with predominant localization on the face and neck, were observed in the majority of the workers.

5. The following array of sanitation measures is required to prevent skin diseases during work with chlorinated diphenyl: 1) provision of protective underwear and outer clothing for the workers; 2) insulation of a shower room of the sanitation control station type, with individual dressing rooms for street clothing and work clothing. The sanitation control station should be outfitted with a steam room for steaming these protective underwear and clothing at a temperature of 110-120° for an hour. The shop should be provided with wash stands with hot and cold water.

6. In order to sanitize the ambient air it is necessary to decrease as much as possible the extent of decomposition of the vinyl chloride resin when subjected to heat treatment. This can be achieved by standardizing its thermal stability, and also by regulating the temperatures to which the rollers, presses, and other equipment are heated, so as to prevent the temperature from exceeding 120-130°.

Of extremely great importance is efficient organization of the ventilation system with the aim of achieving maximum coverage of the sources of liberation of gases, vapors and dust.

In view of the fact that cases of ignition of the condensate form in the ventilation exhaust pipes on contact with open flame have been observed at some plants, in the designing of exhaust systems the specifications given in legislation governing construction for systems designed for the transmission of combustible gaseous mixtures must be complied with.

R&S 110927

PO Box No 6
Bessemer Road
Welwyn Garden City Hertfordshire AL7 1HD
Telephone Welwyn Garden 23400 (STD Code 07073)
Telex 264251
Fax Welwyn Garden 35556 (STD Code 07073)

VCM 0000313



Imperial
Chemical
Industries
PLC

Petrochemicals
and Plastics
Division

Professor C H Tamburro
University of Louisville
School of Medicine
Health Sciences Center
Louisville
Kentucky 40292
USA

cc Dr B Bennett) + copy of
Dr J J O'Sullivan) Tribukh
Dr A P Wright)

~~Dr M N Johnson~~

Dr M N Johnson
File + copy of Tribukh

Your ref

Our ref
JS/LJW/DSO-16

Tel ext
7535

Date
12 January 1983

Dear Professor Tamburro

VCM - ASL CASES

Dr Tim Carter of BP has told me of his telephone conversation with you. I hope that you and Mrs Tamburro will have a comfortable flight and that you will enjoy your weekend in London. I look forward to meeting with you at the Royal College of Pathologists on Monday 24th and again on Tuesday 25th at 9.30 am in Conference Room 01, Imperial Chemical House, Millbank, London. When we are at the Royal College, I shall give you directions to get to IC House.

I understand that you have an arrangement to go to Prof Scheuer at the Royal Free Hospital on Tuesday 25th after our meeting at ICI is finished. If our meeting lasts all morning and you can spare the time, my colleagues and I would be delighted if you would have lunch with us in our mess-room at IC House.

Prof Jenkins has circulated the speakers' summaries. I was interested to read your introductory sentence "In 1949, Tribukh et al first reported hepatitis-like liver changes in vinyl chloride polymerisation workers". Dealing with translations from Russian papers is always a problem. I have usually worked on the basis of the translation of Tribukh made available to the industry by B F Goodrich (copy enclosed). If the translation is accurate, the work is not concerned with VCM polymerisation workers at all and the health effects described are not unequivocally attributable to VCM. The paper is concerned with PVC compounding and fabrication not polymerisation. Though the work done was reasonably good for its time, VCM is not clearly identified, measured or distinguished from chlorinated diphenyls and naphthalenes. Residual vinyl chloride would almost certainly have been evolved from the heated PVC as it was being compounded. The paragraph under Table 2 on p4 asserts that the vapours were "detached molecules of vinyl chloride in various quantitative combinations of their chain compounds". Frankly I don't know what the authors meant to say and perhaps the wording suffers from translation and perhaps also a basic lack of chemical knowledge on the part of the researchers. PVC does not depolymerise to give VCM on being heated. Any VCM given off would be residual VCM in the PVC polymer. If my arithmetic is correct, 1.2 mg/litre is 1200 mg/m³ or 600 ppm in the footwear production rooms. This concentration of VCM is quite astonishing if it all came from residual monomer in PVC. My guess is that the authors could not distinguish between organic chlorine molecules (chlorinated plasticisers etc) and VCM and that the 1.2 mg/l is not VCM pure and simple.

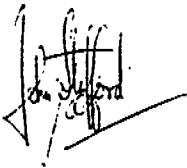
R&S 110928

Unfortunately the Tribukh paper has been abstracted wrongly, eg Abstract 505 p115 of ORNL/TIRC-78/3 (Nov 1978) put out by your National Library of Medicine. Over the years I have given out dozens of copies of the BFG translation of Tribukh and invited people to read it in toto for themselves and to eschew inaccurate abstracts.

I hope you will forgive me for taking up this matter of Tribukh in your summary but I would not want you to legitimise and perpetuate what I believe to be one of the myths in the history of VCM.

With best wishes

Yours sincerely

A handwritten signature in dark ink, appearing to read 'J. Stafford', with a stylized flourish extending from the bottom right.

J Stafford
Health & Environment Protection

R&S 110929

Medizinische Universitätsklinik

Direktor: Professor Dr. H. J. Dengler

VC0000313

5300 Bonn 1, 5th March, 1983

Sigmund-Freud-Str. 25
Rufnummer (0228) 280-1
Durchwahlnummer 280-
Telex 8869545 kib d

Medizinische Universitätsklinik · Sigmund-Freud-Str. 25
5300 Bonn 1

Dr. J. Stafford
Health & Environment Protection
Imperial Chemical Industries
PO Box No. 6
Bessemer Road
Welwyn Garden City
Hertfordshire AL7 1HD
England

R&S 110930

Dear Dr. Stafford,

Thank you very much for your long and detailed letters of February 11 and 18, 1983, and also for your kindness to provide me with a copy of the epidemiological study of respiratory disease ... by SOUTAR et al., 1979, and the two other papers to which I, indeed, had no access at the time when my manuscript was ready for printing. I was glad to learn that you found my paper useful.

In your first letter you raised a crucial question concerning TRIBUKH's early paper. Production (proizvodstvo) of vinyl chloride resins is, indeed, only mentioned in the title and referred to in the opening and introductory paragraphs of this paper, but the 48 male workers examined were said to have been mainly roller operators (preimushchestvenno val'tsovshchiki). It remains unclear whether at this early period the "chlorinated plastizised resin shop" was actually part of a PVC production (polymerization) plant, as the title of the paper suggests. It is also unclear to which plant the authors refer; from subsequent investigations of environmental conditions in PVC production carried out by SMIRNOVA (1954, paper mentioned by FILATOVA) and later by FILATOVA et al. (1958), I thought it likely that TRIBUKH's paper also dealt with the Gor'kii combinat where apparently all of the Russian work on adverse effects of vinyl chloride up to the present (see FILATOVA et al., Gig. Tr. Prof. Zabol. no. 1, January 1982, pp. 28-31) has been conducted. I used a photocopy of TRIBUKH's original Russian paper and since I have some very limited knowledge of Russian I tried to translate the article with the help of a slavacist from the Slavistic Seminar of our University, who, however, was not versed with the technical and medical terminology which I had to provide. From the English translation which you kindly sent me I can see, however, that the two translations are practically identical.

You will have noticed that in my paper (see page 44) I accentuated that the group of 73 workers examined were "mainly engaged in PVC compounding". I interpreted TRIBUKH's statement that "the

R&S 110931

organic chlorine compounds evolved in the heat treatment of the vinyl chloride resins are detached molecules of vinyl chloride" to mean that unreacted monomer was released by the heating process (and we know well enough that in those early days PVC resins did contain considerable amounts of unreacted monomer, especially when the freshly polymerized resins were immediately used for processing without intermediate storage). I also accentuated that the authors "held other volatile compounds derived from halogenated aromatic hydrocarbons (...) ... responsible for the systemic toxicity".

All this goes to show that I too had some doubts as to the substantiation of the title's claim; however, I have not been able to unearth any earlier hint or warning from the world literature, weak as this one (TRIBUKH's paper) may have been.

But on second thought I admit that you are probably quite justified to repudiate TRIBUKH's claim concerning production of PVC. For your information I include a photocopy of my original copy of this paper which was published in "Gigiena i Sanitaria", issue no. 10, October 1949, pp. 38-44 (not: "Arg. Sanit." vol. 10, pp. 38-45). I further include a photocopy of SMIRNOVA's paper (Gor'kii combinat) who was actually the first author to describe occupational acroosteolysis in one fitter and two centrifuge operators in 1961, five years before this type of VC-induced lesion was recognized in Europe.

You also inquired about the ASL case described in my paper in fig. 6 a+b (pp. 56 + 57). You were right, he did not die in June 1978 but on the 28th of August 1978, two days before we expected him to show up at our clinic to have a computerized tomography of the liver because during a short stay at our clinic in early August 1978 the clinical examination led us to suspect that angiosarcoma of the liver was developing. His (A.W.) birth date was the 6th June 1937; these data, I hope, will make it possible for you to identify this case of ASL in your register (Dynamit Nobel).

I apologize for the delay in answering your letters, but even today it takes me some time to formulate my words in a foreign language.

With kind regards and best wishes.

Yours sincerely,



Prof. Dr. W.K. Leibach

N.B. for ASL case file

* CASE 17

INITIALS — A.W.

D.O.B. — 6 June 1937

BFC
request to
omit
initials
+
names
+
dates
DOB.

CASE
17
MY
REPLY